

Rate and Cycling Performance of Ti and Cu Doped β -NaMnO₂ as Cathode of Sodium-ion Battery

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Abstract: Sodium-ion batteries are economical and environmentally sustainable energy storage batteries. Among them, β -NaMnO₂, a promising sodium-ion cathode material, is a manganese-based oxide with a corrugated laminar structure, which has attracted significant attention due to its structural robustness and relatively high specific capacity. However, it has short cycle life and poor rate capability. To address these issues, Ti atoms, known for enhancing structural stability, and Cu atoms, which facilitate desodiation, were doped into β -NaMnO₂ by first-principles calculation and crystal orbital Hamilton population (COHP) analysis. β -NaMn_{0.8}Ti_{0.1}Cu_{0.1}O₂ exhibits a notable increase in reversible specific capacity and remarkable rate properties. Operating at a current density of 0.2C (1C = 219 mA·g⁻¹) and within a voltage range of 1.8–4.0 V, the modified material delivers an initial discharge capacity of 132 mAh·g⁻¹. After charge/discharge testing at current densities of 0.2C, 0.5C, 1C, 3C, and 0.2C, the material still maintains a capacity of 110 mAh·g⁻¹. The doping of Ti atoms slows down the changes in the crystal structure, resulting in only minimal variation in the lattice constant c/a during the desodiation process. Mn and Cu engage in reversible redox reactions at voltages below 3.0 V and around 3.5 V, respectively. The extended plateau observed in the discharge curve below 3.0 V signifies that Mn significantly contributes to the overall battery capacity. This study provides insights into modifying β -NaMnO₂ as a cathode material, offering experimental evidence and theoretical guidance for enhancing battery performance in Na-ion batteries.

Key words: first-principles; sodium-ion battery; layered cathode material

Sodium-ion battery is an emerging battery technology that utilizes the mutual transfer of sodium ions between positive and negative electrodes to store and release electrical energy^[1]. Compared to lithium, sodium is an abundant element in the earth's crust and is more widely available and cheaper^[2-3]. This indicates that the raw materials for sodium-ion batteries are more abundant and can be manufactured on a larger scale, leading to reduced battery costs and enhanced sustainability^[4]. In addition, the larger and more stable ionic size of sodium compared to lithium ion reduces stress and loss within the battery, thereby extending battery's life^[5]. Therefore, sodium-ion

batteries have a longer cycle life and better low-temperature performance^[6].

The cathode materials for sodium-ion batteries include oxides, polyanions, Prussian blue and organic materials^[7-10]. Among them, oxides have the advantages of simple preparation, high specific capacity and good electrical conductivity compared with other types^[11]. One particular material of interest is NaMnO₂, which exhibits the unique zig-zag layered structure known as β phase in addition to the O3 layered structure referred to as α phase^[12-13]. The space group of this material is denoted as Pmmn, wherein sodium ions are arranged in a corrugated

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manner between the layers of transition metal. Notably, the β -NaMnO₂ phase, also known as the high-temperature (HT) phase, demonstrates superior cycling performance and rate capability compared to its low-temperature counterpart, α -NaMnO₂^[14]. β -NaMnO₂ seldomly exists in a pure phase form and, in general, exists in a complex phase with α -NaMnO₂^[15]. Leveraging the doping effect was proved a successful approach for enhancing the electrochemical characteristics of electrode materials^[16–18]. Density functional theory (DFT) calculations by Shishkin *et al.*^[19] revealed that Cu doping favors the formation of the β -phase. The pure β -phase NaCu_{0.1}Mn_{0.9}O₂ can be obtained by Cu doping and sintering in air^[20]. In comparison to α -NaMnO₂, the Jahn-Teller distortion due to the oxidation states of Mn³⁺/Mn⁴⁺ can be reduced in β -NaMnO₂^[21]. Therefore, a new material with β -NaMnO₂ structure is of great significance for the design of high-performance sodium-ion cathode materials.

In summary, although several studies have aimed at optimizing the performance of β -NaMnO₂ as a battery cathode material, there remains a paucity of research focused on enhancing its electrochemical performance and structural stability through dual-element co-doping. Particularly, the methodologies for the screening of doping elements are still underdeveloped. In this study, first-principles calculations and crystal orbital Hamilton population (COHP) analysis were employed to devise a screening strategy for identifying suitable dopants, selecting Ti and Cu based on the differing COHPs of TM–O and Na–O bonds among various transition metals. Ti enhances the structural stability of the crystal, while Cu facilitates the insertion and extraction of sodium ions. Three variants of β -NaMnO₂ with different doping ratios were synthesized, and their crystal structures, morphological features, and electrochemical properties were thoroughly investigated.

1 Experimental and computational methods

1.1 Material synthesis

The chemicals used in this study were of analytical purity and obtained from Aladdin Biochemical Technology. The synthesis of β -MTC811 involved a solid-state reaction method. To ensure thorough mixing, Na₂CO₃, Mn₂O₃, TiO₂ and CuO powders were milled together for 30 min under ambient air conditions. The resulting precursors were then pressed into pellets under a pressure of 10 MPa. Subsequently, the pellets were subjected to calcination in a helium atmosphere at 900 °C for 15 h. The heating rate during calcination was controlled at 5 °C/min to

ensure a gradual and uniform temperature increase. After calcination, the samples were naturally cooled to room temperature. To facilitate further experimentation, the calcined pellets were promptly milled into fine powders and transferred into an argon-filled glove box to prevent any undesired reactions or contamination. The synthesis for β -MTC721 and β -MTC712 followed similar steps with different chemicals and stoichiometry.

1.2 Material characterization

The crystalline structure of the sample was thoroughly examined using X-ray diffraction (XRD, D8 ADVANCE) analysis, employing Cu K α radiation at a wavelength of 0.15418 nm, a scanning range of $2\theta=10^{\circ}$ – 80° , and a controlled scan speed of 5 (°)/min. To gain insights into the morphology of the sample, scanning electron microscopy (SEM, ZEISS Sigma 300) and transmission electron microscopy (TEM, JEOL JEM-2100Plus) were employed. Furthermore, to investigate the elemental distribution of the sample, energy dispersive spectroscopy (EDS) was employed. In order to elucidate any potential valence changes exhibited by the elements in different states, X-ray photoelectron spectroscopy (XPS) was employed using a state-of-the-art Thermo Scientific K-Alpha instrument equipped with Al K α radiation.

1.3 Electrochemical measurement

Coin cells (CR2032) were meticulously assembled within an argon-filled glove box. The electrodes were prepared by mixing active material, carbon black and polyvinylidene fluoride (PVDF) with *N*-methylpyrrolidone (NMP). This paste was then coated onto aluminum foil substrates and vacuum dried at 100 °C for 12 h. Na metal sheets and glass fibers were used as the anode and diaphragm, respectively. 1 mol/L NaClO₄ EC/EMC/DMC (1 : 1 : 1 (in volume)) solution was employed as electrolyte. Charge/discharge measurements were performed using a battery test system (CT-3002A, LAND). Cyclic voltammetry (CV) test was carried out on an electrochemical workstation (Metrohm-Autolab, PGSTAT 302N).

1.4 Density functional theory calculations

In this study, DFT calculations were conducted using the Vienna *ab initio* Simulation Package (VASP) to investigate intercalation processes in batteries^[22]. The Perdew-PBE exchange-correlation function within the generalized gradient approximation (GGA) was employed to describe the electron exchange-correlation energy^[23]. The projector-augmented-wave (PAW) method with a cut-off energy of 600 eV was utilized for accurate electronic structure calculations. To efficiently sample the Brillouin zone, a Monkhorst-Pack scheme with a 3×3×2 grid was used for *k*-point sampling^[24]. Additionally, a supercell program was employed to explore structures

with different sodium contents during the desodiation process^[25]. Furthermore, COHP analysis using the LOBSTER package was performed to gain insights into chemical bonding and interatomic interactions^[26-27]. To analyze the charge transfer, the Bader charge was calculated^[28-29]. All crystal structure schematics were produced using VESTA software^[30].

2 Results and discussion

2.1 Elemental screening

To ascertain the potential of transition metal doping to enhance the stability of β -NaMnO₂ structure and facilitate the extraction of sodium ions, the bonding strengths of TM–O (TM=Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) and Na–O (O from Na–O–TM) within the β -NaMnO₂ lattice with varying 3d transition metal dopants were firstly calculated. As shown in Fig. 1(a), for simplification, the crystal structure of the 3d transition metal single-atom replacing the Mn position in β -NaMnO₂ was calculated without considering the influence of doping concentration. Subsequently, the COHP values for the doped structures were determined with particular emphasis on negative values indicating bonding interactions. In addition, ICOHP represents the integrated COHP from the lowest energy level to the Fermi energy level, serving as a measure of the bonding

strength between two atoms. The results of all –ICOHP and –COHP for TM–O and Na–O of single TM atom doped β -NaMnO₂ are presented in Fig. 1(b), Fig. S1 and Fig. S2. The single Cu atom doped structure possesses the lowest –ICOHP value of Na–O, indicating that the doping of Cu attenuates the bonding strength between the oxygen (O from Na–O–Cu) and sodium atoms (Fig. 1(b, c)). Among the nine calculated transition metals, Na–O (in Na–O–Cu) possesses the longest bond length (Table S1), corresponding to the smallest bond energy, implying that Cu doping favors the weakening of Na–O bond. This weakened Na–O bond facilitates bond cleavage during the charging process, thereby favoring the extraction of sodium ions from the structure. Consequently, Cu doping is anticipated to enhance the rapid reaction kinetics of sodium ions and confer high rate properties to the material.

In addition, it is found that the Ti doped β -NaMnO₂ structure has the highest –ICOHP of Ti–O (Fig. 1(b, d)), indicating the formation of the strongest Ti–O bond when Ti replaces Mn among all doped 3d transition metals. In the bond length statistics, considering the price and environmental factors, excluding Ni and Co, the Ti–O bond has the shortest bond length (Table S1). It is widely recognized that a strong TM–O bond enhances the ability of batteries to maintain structural stability throughout charging and discharging cycles. Consequently, this substitution is anticipated to positively contribute to

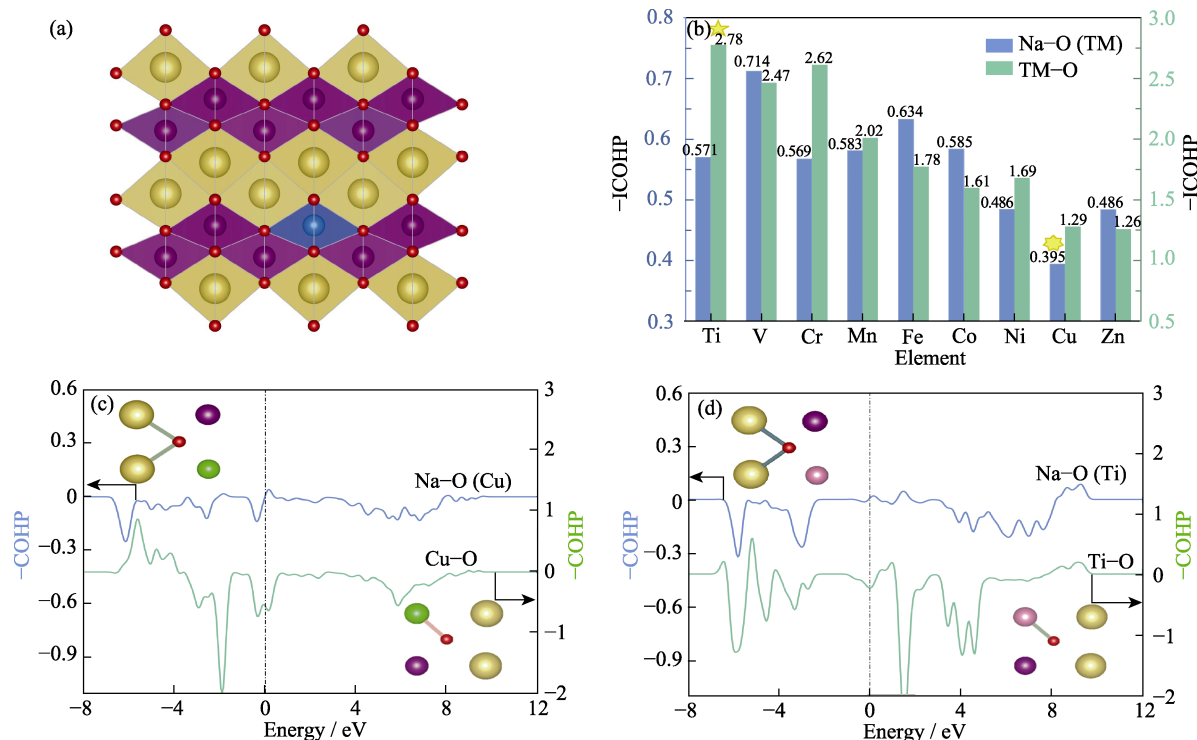


Fig. 1 Screening of doped atoms in β -NaMnO₂

(a) Schematic crystal structure of β -NaMnO₂ doped by 3d transition metal atoms; (b) –ICOHP of Na–O and TM–O (TM=Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn); (c) –COHP of Na–O and Cu–O in Cu doped β -NaMnO₂; (d) –COHP of Na–O and Ti–O in Ti doped β -NaMnO₂. Colorful figures are available on website

upholding the structural stability of the electrode material during charge-discharge processes. Taking into consideration of both aspects of rate performance and structural stability, Ti and Cu elements are selected as potential substitutes for a portion of Mn in β -NaMnO₂. These substitutions are anticipated to enhance both bonding strength and structural integrity, thereby improving overall battery performance.

2.2 Structural characterization

Based on the results of high-throughput screening of doped atom species, Ti and Cu co-doped β -NaMnO₂ structure was synthesized using the solid-phase method. Given that doping concentration influences the electrochemical properties of the material, three different materials with distinct ratios of Mn : Ti : Cu were synthesized. A comprehensive investigation was conducted to determine the stoichiometry of the synthesized compounds, employing inductively coupled plasma optical emission spectrometry (ICP-OES). The analysis reveals that the ratios of Mn : Ti : Cu were 8 : 1 : 1, 7 : 1 : 2 and 7 : 2 : 1, denoted as NaMn_{0.8}Ti_{0.1}Cu_{0.1}O₂ (β -MTC811), NaMn_{0.7}Ti_{0.1}Cu_{0.2}O₂ (β -MTC712) and NaMn_{0.7}Ti_{0.2}Cu_{0.1}O₂

(β -MTC721).

Based on the elemental stoichiometry obtained from ICP-OES (Table S2), the crystal structure (Fig. 2(a)) with the lowest energy for β -MTC811 is identified through a two-step calculation process, involving initial screening of Coulombic interactions followed by more accurate DFT calculations. The consistency between the experimental and calculated XRD diffraction peaks of β -MTC811 (Fig. 2(b)) confirms the successful synthesis of β -MTC811. Additionally, β -MTC811 features with Pmmn symmetric rhombohedral lattice and characteristic of the β -type structure, similar to β -MTC712 and β -MTC721 (Fig. S3). Moreover, in all three materials, the doping sites of the dopant elements Ti and Cu are close to each other (Fig. 2(a) and Fig. S4). To gain deeper insights into the morphology and structure of the synthesized material, SEM is employed and presented in Fig. 2(c). Remarkably, SEM images reveal a distinctive rod-like morphology instead of the anticipated layered arrangement commonly observed in similar materials^[20, 31]. Furthermore, EDS elemental mappings done by STEM techniques are conducted to

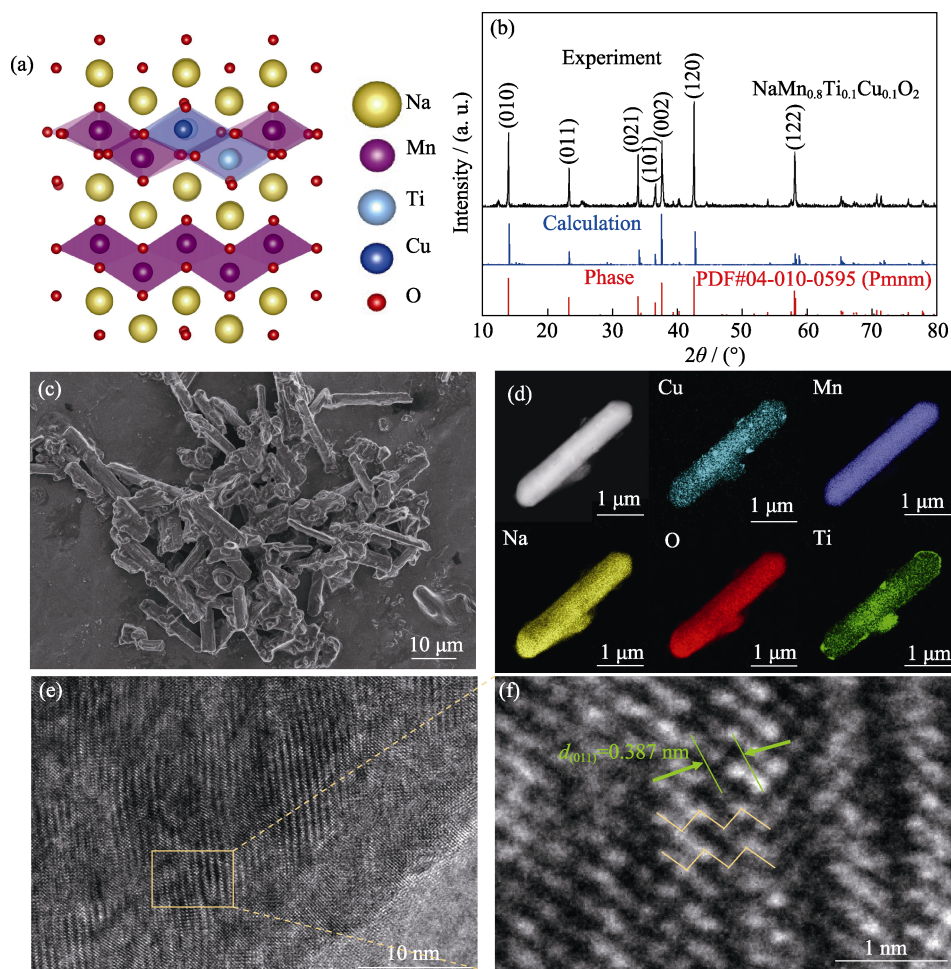


Fig. 2 Structure and morphology of β -MTC811

(a) Crystal structure modeling of β -MTC811 that obtained by calculation; (b) Comparison of calculated and experimental XRD patterns of β -MTC811; (c) SEM image of β -MTC811; (d) EDS mappings of β -MTC811; (e) TEM image of β -MTC811; (f) Enlarged image of zig-zag layered structure in (e)

investigate the distribution of elements within the sample. The results obtained from EDS analysis in Fig. 2(d) confirm the presence of Na, Mn, Ti, Cu, and O elements throughout the sample. Notably, the lower content of Ti and Cu compared to Mn indicates their partial substitution within the lattice structure. The structure of β -MTC811 was analyzed by TEM as shown in Fig. 2(e). In the enlarged image (Fig. 2(f)), the zig-zag layered structure can be clearly observed, which coincides with the XRD characterization results. The space distance (0.387 nm) is ascribed to the characteristic crystalline surface (011) of the β -phase.

2.3 Electrochemical performance

To determine the optimal doping ratio for the electrochemical performance, the cathodes β -MTC811, β -MTC721, and β -MTC712 were assembled with sodium metal to afford half-cells (Table S3), and their electrochemical performances are characterized under identical testing conditions. The obtained charge/discharge curves of β -MTC811, β -MTC721, and β -MTC712 were plotted within the voltage range of 1.8–4.0 V at a current density of 0.2C. As shown in Fig. 3(a-c), when first charging to 4.0 V and discharging to 1.8 V, the charge/discharge specific capacities of β -MTC811, β -MTC721 and β -MTC712 are 108.83/132, 108.16/99 and 110.12/88 mAh·g⁻¹, respectively, corresponding to first Coulombic efficiencies of 121.29%, 91.53% and 79.91%. Furthermore, the discharge specific capacities of three cathode materials are 112, 81 and 80 mAh·g⁻¹ at the end of the 20th cycle, demonstrating that Mn : Ti : Cu ratio of 8 : 1 : 1 can achieve high discharge specific capacity of doped β -NaMnO₂, and Mn is presented as a major contributor

to capacity. Even after 50 cycles (Fig. 3(d)), β -MTC811 still has a higher specific capacity than those of β -MTC721 and β -MTC712 (Fig. S5), demonstrating that β -MTC811 has good structural stability. β -MTC721 and β -MTC712 cathodes (Fig. S5) also maintain the initial specific capacity (90 and 81 mAh·g⁻¹) when cycled multiple times at 0.2C, 0.5C, 1C, 3C and then returned to 0.2C. Compared to them, the reversible capacities of β -MTC811 (Fig. 3(e)) are optimal (110 mAh·g⁻¹). The dQ/dV curves (Fig. 3(f)) provide further insights, revealing two pairs of redox peaks within the potential range of 1.8–4.0 V. The oxidation and reduction peaks occur at 2.8/2.4 V and 3.62/3.34 V, respectively, corresponding to the redox reaction of Mn³⁺/Mn⁴⁺ and Cu²⁺/Cu^{2+x} during charge and discharge. The presence of two pairs of peaks ascribed to the redox of Mn and Cu can also be seen in the CV test (Fig. S6). The peak current of Mn is higher than that of Cu, indicating that the redox rate of Mn is greater than that of Cu.

2.4 Charge compensation mechanism

To elucidate the redox mechanism of the cathode material β -MTC811, XPS was performed at different charging and discharging states. The core spectra of Mn2p and Cu2p for the synthesized β -MTC811 are presented in Fig. 4. The Mn2p_{3/2} and Mn2p_{1/2} peaks (Fig. 4(a)), observed at binding energies of 641.5 and 652.9 eV, respectively, are indicative of Mn³⁺[32]. Additionally, two peaks at 642.5 and 654.3 eV indicate the presence of Mn⁴⁺. More importantly, the content of Mn³⁺ in the initial β -MTC811 structure is much higher than that of Mn⁴⁺. Upon charging to 3.0 V, a noticeable decrease in Mn³⁺ content and an increase in Mn⁴⁺ content are observed, indicating

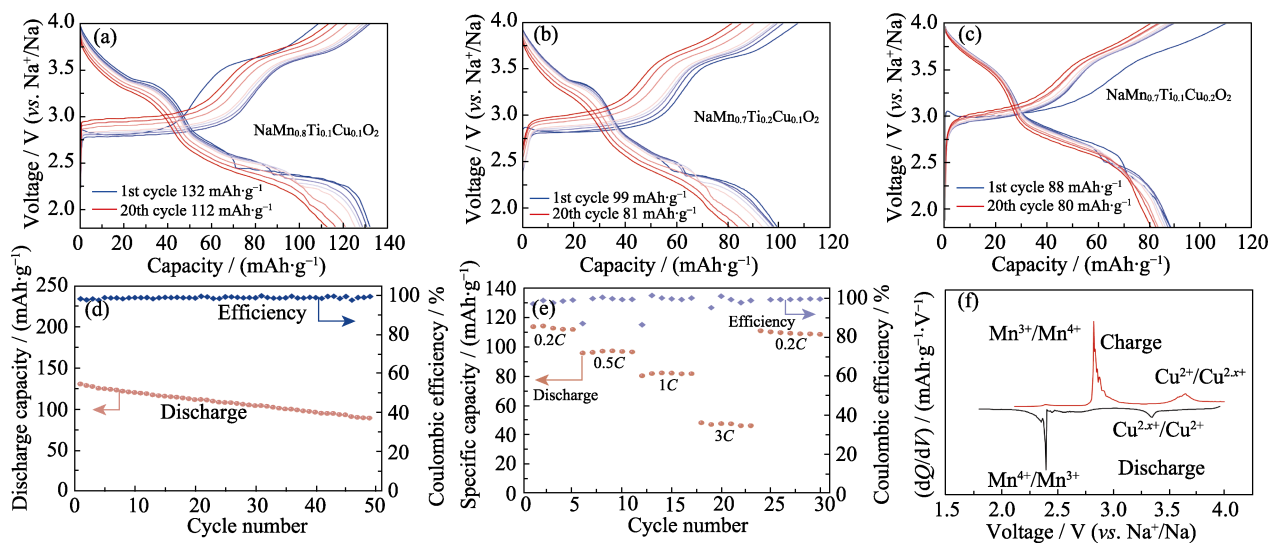


Fig. 3 Electrochemical performance of β -MTC811 cathode
(a-c) Charge/discharge curves of (a) β -MTC811, (b) β -MTC721 and (c) β -MTC712 at 0.2C; (d) Cycling performance, (e) rate performance and (f) dQ/dV curves of β -MTC811
Colorful figures are available on website

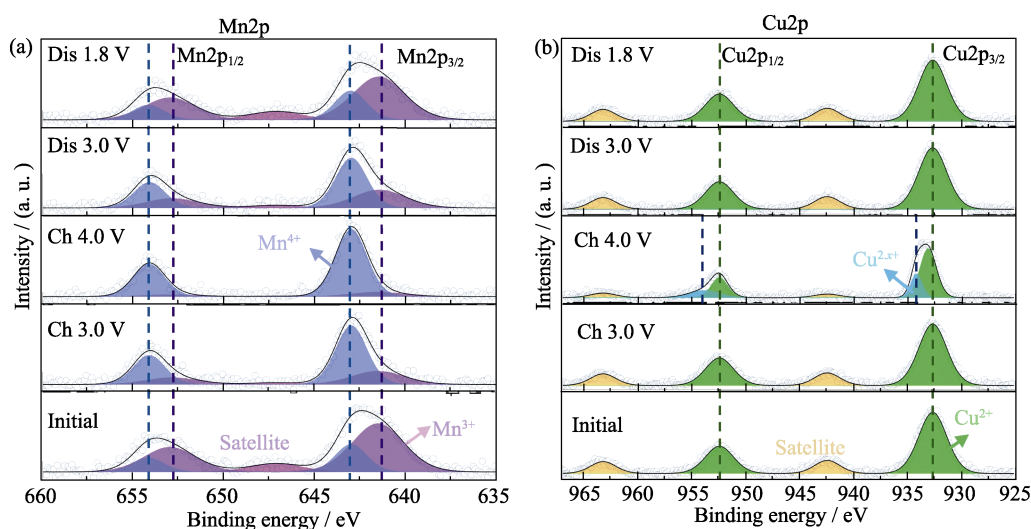


Fig. 4 Electrochemical reaction mechanisms

(a) Mn2p and (b) Cu2p XPS spectra of β -MTC811 in different charging and discharging states. Colorful figures are available on website

the oxidation of Mn^{3+} . With charging to 4.0 V, almost all characteristic peaks associated with Mn^{3+} disappear, while only peaks corresponding to Mn^{4+} exist, suggesting that nearly all Mn ions are oxidized to Mn^{4+} . During the subsequent discharge process, a small amount of Mn is reduced back to the Mn^{3+} . Remarkably, upon discharging to 1.8 V, the contents of Mn^{4+} and Mn^{3+} in the cathode material remain unchanged from the initial state, providing evidence for the electrochemical activity of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. In $\text{Cu}2\text{p}_{3/2}$ XPS spectra (Fig. 4(b)), a peak at 933.5 eV and a satellite peak near 942.0 eV are ascribed to Cu^{2+} ^[33]. During charging to 3.0 V, Cu^{2+} is hardly oxidized, as evidenced by the absence of significant changes in the core spectrum. However, upon charging to 4.0 V, the core spectrum of Cu^{2+} splits into two distinct peaks, accompanied by a decrease in intensity of the satellite peak associated with Cu^{2+} . These observations suggest that a fraction of Cu^{2+} undergoes oxidation within the voltage range of 3–4 V. Upon discharging to 3.0 V, the split peak in the $\text{Cu}2\text{p}_{3/2}$ spectrum vanishes, and the satellite peak associated with Cu^{2+} reappears simultaneously, indicating that a portion of oxidized Cu undergoes reduction during this discharge process. Thus, based on dQ/dV curves and XPS characterization, it has been established that β -MTC811 cathode material undergoes redox reactions involving $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Cu}^{2+}/\text{Cu}^{2+x+}$ couples during electrochemical cycling.

In order to comprehensively understand the underlying mechanism of the electrochemical reaction in batteries, first-principles calculations were performed on β -MTC811. The crystalline cell parameters of β -MTC811 structure are calculated as $a=4.775$ Å, $b=2.858$ Å, $c=6.339$ Å, and $\alpha=\gamma=\beta=90^\circ$, which indicate an orthorhombic system with the Pmmn space group. During the desodiation process, a

periodic Coulomb energy approach was employed to analyze desodiated sites and desodiation-driven structural changes. The structural evolution depicted in Fig. 5(a) reveals that sodium ions surrounding Cu are initially dislodged from the structure, indicating the weakening O–Na (O from Cu–O–Na) bond strength due to Cu doping. Even after the removal of half of the sodium ions, $\beta\text{-Na}_{0.5}\text{Mn}_{0.8}\text{Ti}_{0.1}\text{Cu}_{0.1}\text{O}_2$ still retains the symmetry of its original structural framework, corresponding to a theoretical specific capacity of $130 \text{ mAh}\cdot\text{g}^{-1}$, which closely matches the reversible specific capacity observed in experiments. It is observed that the lattice constant c/a in Fig. 5(b) does not change significantly during the desodiation process, indicating that the structure of the material remains relatively stable as the chemical reaction proceeds. Using the change of Gibbs free energy, charge voltages of β -MTC811 are calculated with reference to Na metal by using the formula (1)^[34].

$$V = \frac{E_{\beta\text{-Na}_x\text{MTC811}} - nE_{\text{Na}} - E_{\beta\text{-Na}_{x-n}\text{MTC811}}}{-ne} \quad (1)$$

Where n denotes the number of sodium ions removed, and $E_{\beta\text{-Na}_x\text{MTC811}}$ (eV) and $E_{\beta\text{-Na}_{x-n}\text{MTC811}}$ (eV) denote the formation energy before and after the removal of n sodium ions, respectively. E_{Na} (eV) is the formation energy of sodium. Within the crystal cell, there are initially 24 Na ions, and 2 Na ions are successively removed every time until 12 Na ions remain. In accordance with the experimental charging curves, calculations reveal the presence of two distinct voltage plateaus. Specifically, the oxidation reaction of Mn occurs between 2.5 and 3.0 V during the process from 0.9 to 0.7 Na^+ , while the oxidation reaction of Cu takes place between 3.0 and 3.5 V during the process from 0.7 to 0.5 Na^+ (Fig. 5(c)). Remarkably, the computational results exhibit agreement

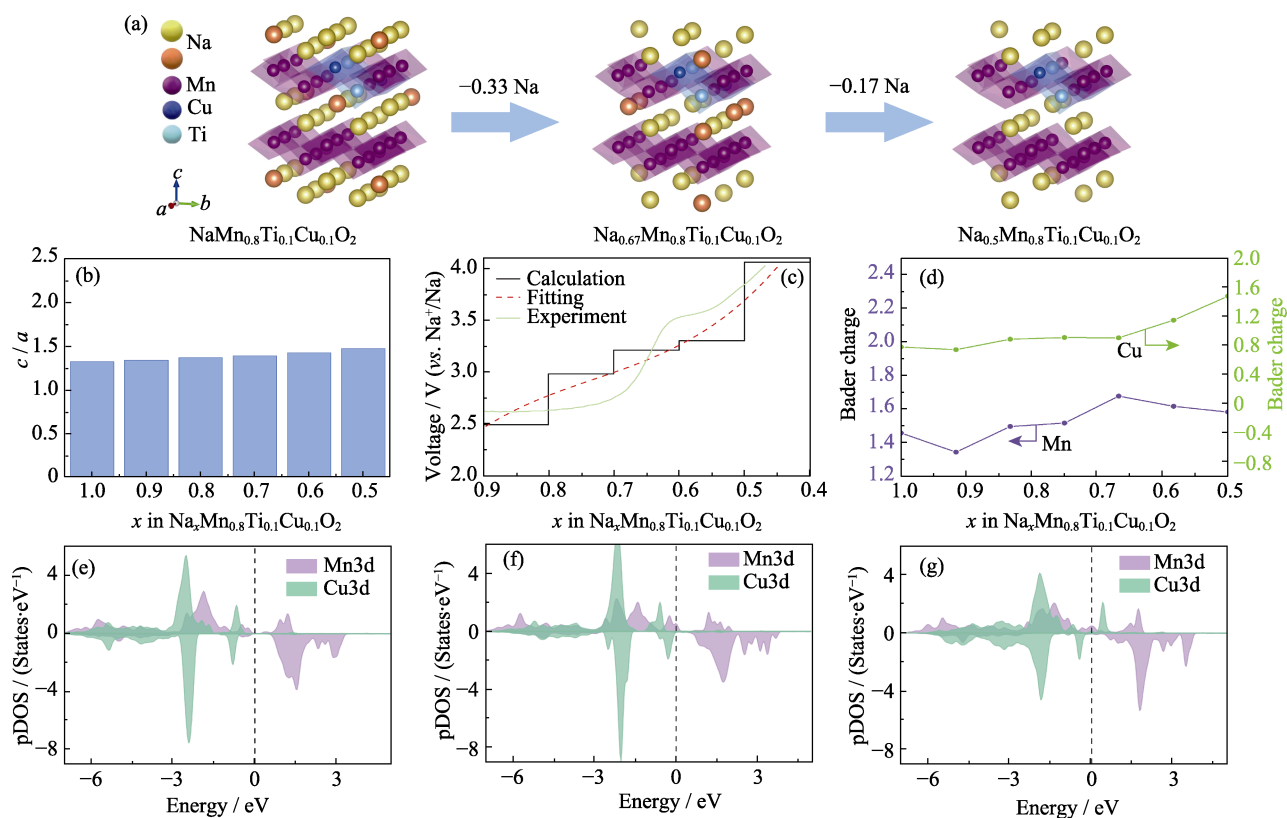


Fig. 5 First-principles calculations of β -MTC811 cathode

(a) Schematic diagram of desodiation process; (b) Lattice constant c/a during desodiation; (c) Calculated and fitted voltage plateaus, and experimental voltage curve; (d) Bader charge of Mn and Cu; (e-g) pDOS of Mn3d and Cu3d during different desodiation processes

Colorful figures are available on website

with experimental observations^[35].

Furthermore, analysis of the Bader charges for the transition metals Mn and Cu was conducted throughout the desodiation process (Fig. 5(d)). Notably, it is observed that there is a general increase in the valence states of these elements as sodium ions removed from the structure. To gain further insights, a detailed examination of the partial density of states (pDOS) for Mn3d and Cu3d in β -MTC811 was performed (Fig. 5(e-g)). During desodiation, the 3d orbitals of Mn gradually shift towards higher energy levels, eventually crossing the Fermi energy threshold. This observation strongly suggests that Mn exhibits electrochemical activity during this process. Similarly, the removal of Na ions is attributed to the shift of Cu3d orbitals towards higher energy levels. Significantly, these unoccupied orbitals of Cu extend beyond the Fermi energy level, providing additional evidence for an elevated valence state and electrochemical activity of Cu.

3 Conclusions

In summary, this study unveils the promising potential of β -NaMnO₂ as a cathode material for sodium-ion batteries. Through first-principles calculations screening, Ti was identified for structural stability and Cu for

facilitating sodium ion de-embedding, thereby enhancing the cyclic stability and rate performance of β -NaMnO₂. Furthermore, the Ti and Cu co-doped pure-phase structure of β -NaMn_{0.8}Ti_{0.1}Cu_{0.1}O₂ was synthesized by the solid-phase method. The material exhibited an impressive initial discharge capacity of 132 mAh·g⁻¹ under specific operating conditions, higher than those of β -MTC721 (99 mAh·g⁻¹) and β -MTC712 (81 mAh·g⁻¹). XPS and DFT analyses further confirmed the significant contributions of Mn and Cu to the electrochemical activity of the modified cathode material. These insights offer valuable guidance for the design and optimization of cathode materials for Na-ion batteries, bridging experimental evidence with theoretical understanding to propel future advancements in battery performance.

Supporting materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20240204>.

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Ti 和 Cu 掺杂 β -NaMnO₂ 正极材料： 钠离子电池的倍率和循环性能

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摘要: 钠离子电池是一种经济且环境可持续的储能电池。其中, β -NaMnO₂ 作为前景广阔的钠离子正极材料, 是一种具有波纹形层状结构的锰基氧化物, 因其结构坚固和比容量相对较高而备受关注。然而, β -NaMnO₂ 存在循环寿命短、倍率性能不佳的问题。为了解决这些问题, 本研究通过第一性原理计算和晶体轨道哈密顿布局(COHP)分析, 在 β -NaMnO₂ 中掺入了可以提高材料结构稳定性的 Ti 原子和有利于钠离子脱出的 Cu 原子。 β -NaMn_{0.8}Ti_{0.1}Cu_{0.1}O₂ 的可逆比容量显著增长, 并且具有卓越的倍率性能。在 0.2C 电流密度($1C=219\text{ mA}\cdot\text{g}^{-1}$)、1.8~4.0 V 电压范围内, 改性材料的初始放电比容量为 $132\text{ mAh}\cdot\text{g}^{-1}$ 。分别在 0.2C、0.5C、1C、3C 和 0.2C 的电流密度下进行充放电测试后, 该材料仍能保持 $110\text{ mAh}\cdot\text{g}^{-1}$ 的比容量。掺入 Ti 减缓了晶体结构的变化, 晶格常数 c/a 在脱钠过程中仅有微小变化。Mn 和 Cu 分别在 3.0 V 以下和 3.5 V 左右发生可逆氧化还原反应, 在放电曲线中, 3.0 V 以下的长平台表明 Mn 是电池容量的主要贡献者。本工作深入研究了改性 β -NaMnO₂ 正极材料的工作机理, 为提高钠离子电池的性能提供了实验依据和理论指导。

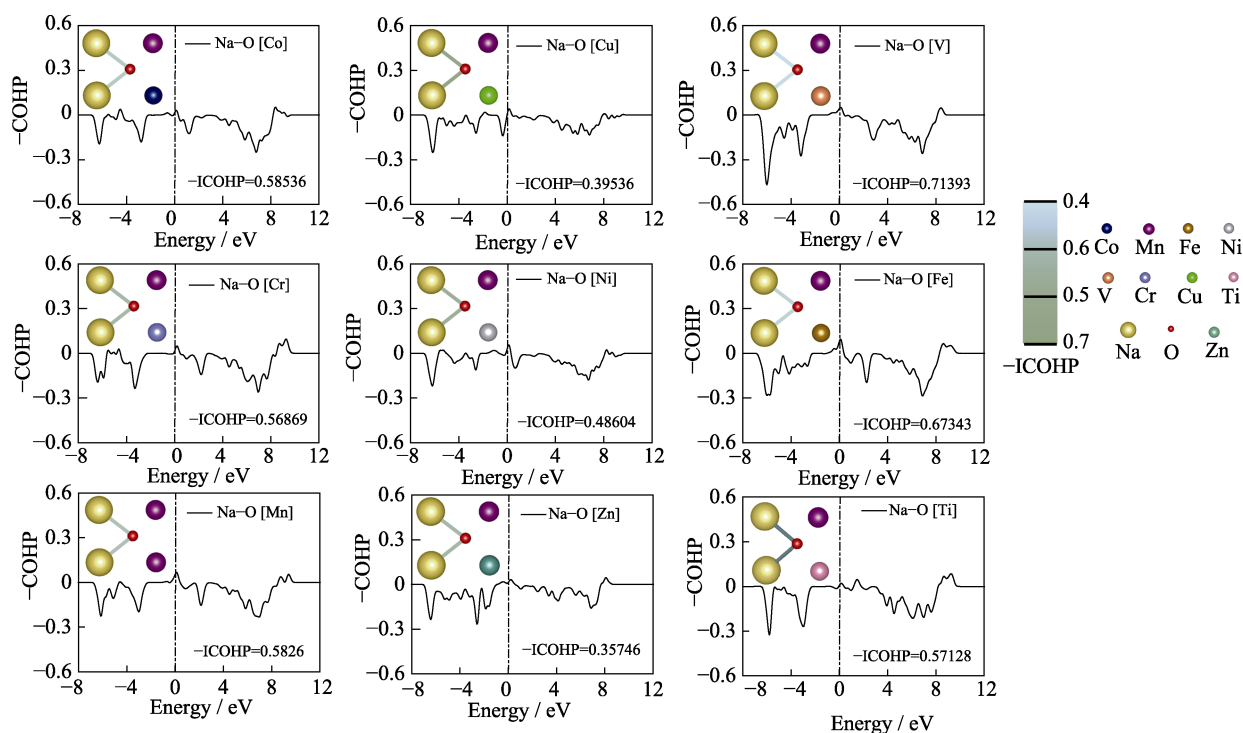
关键词: 第一性原理; 钠离子电池; 层状正极材料

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Supporting Information:

Ti and Cu Doped β -NaMnO₂ as Cathode of Sodium-ion Battery: Rate and Cycling PerformanceZHOU Jingyu^{1,2,3}, LI Xingyu², ZHAO Xiaolin^{2,3}, WANG Youwei^{2,3}, SONG Erhong^{2,3}, LIU Jianjun^{1,2,3}

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Fig. S1 -COHP of Na-O (O from Na-O-TM) (TM=Co, Cu, V, Cr, Ni, Fe, Mn, Zn, Ti) in doped β -NaMnO₂

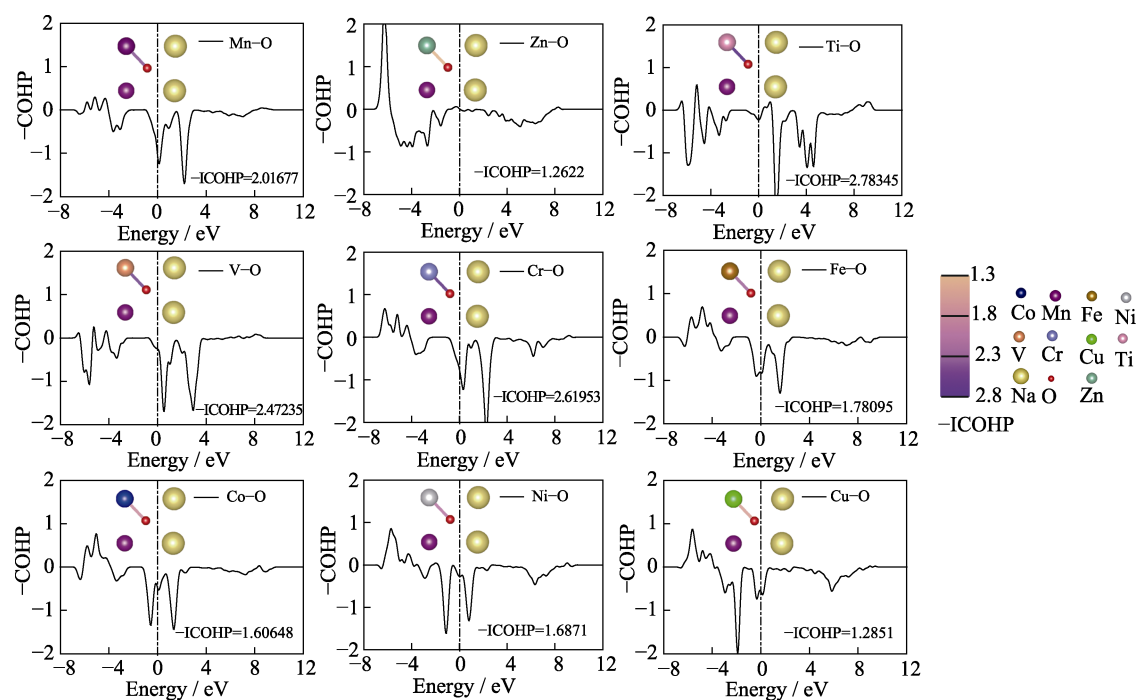


Fig. S2 $-\text{COHP}$ of TM-O ($\text{TM}=\text{Mn}, \text{Zn}, \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) in doped $\beta\text{-NaMnO}_2$

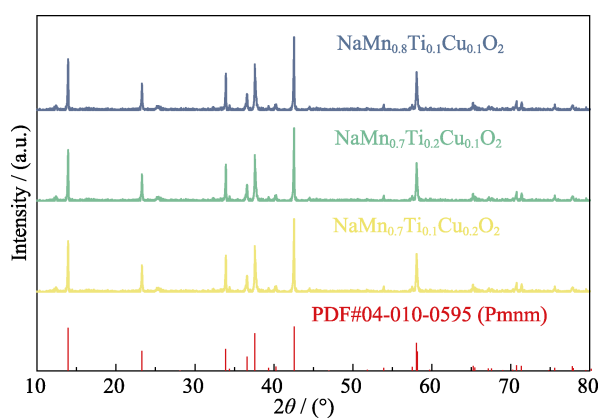


Fig. S3 XRD patterns of $\beta\text{-MTC811}$, $\beta\text{-MTC721}$ and $\beta\text{-MTC712}$

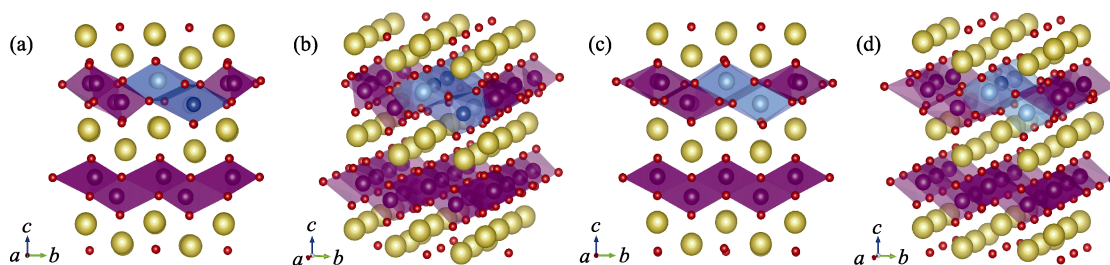


Fig. S4 Crystal-structure modelings of (a, b) $\beta\text{-MTC712}$ and (c, d) $\beta\text{-MTC721}$

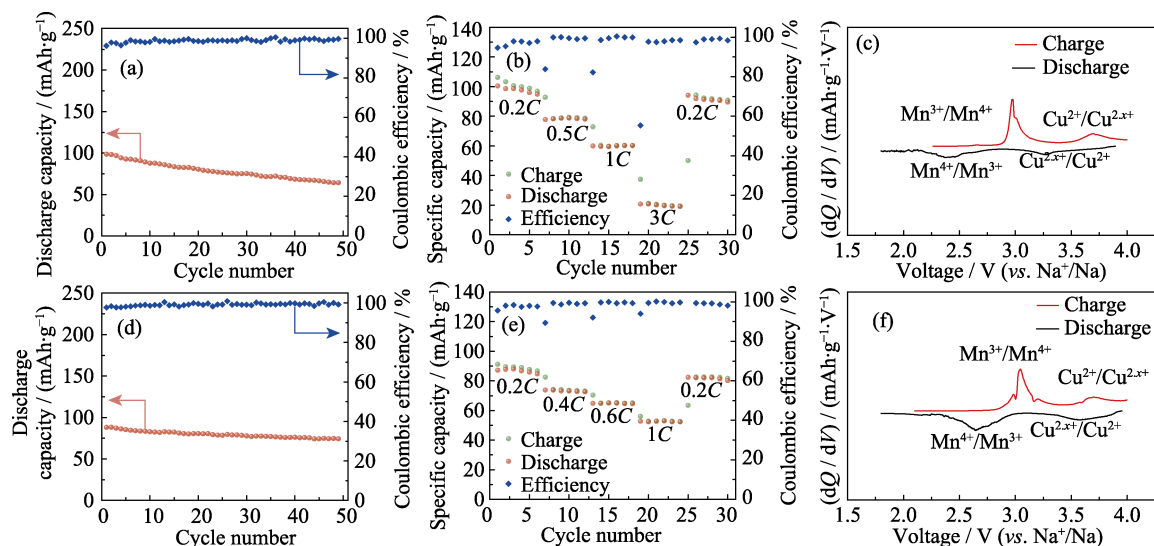


Fig. S5 Electrochemical performance of (a-c) β -MTC721 and (d-f) β -MTC712 cathodes
(a, d) Cycling performance during 50 cycles; (b, e) rate performance; (c, f) dQ/dV curves

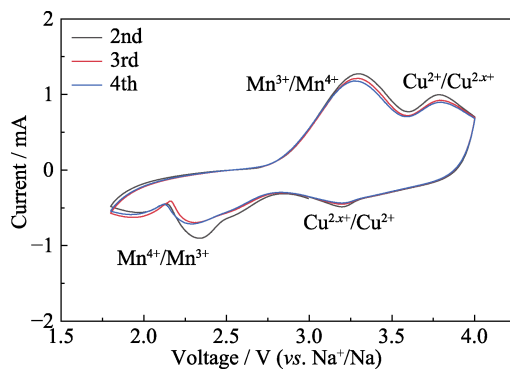


Fig. S6 CV curves of β -MTC811

Table S1 Bond lengths of Na–O (in Na–O–TM) and TM–O

Element	Na–O/Å	TM–O/Å
Ti	2.37641	1.95505
V	2.32810	1.98783
Cr	2.36871	1.98479
Mn	2.33621	1.97821
Fe	2.34627	2.00070
Co	2.36626	1.94259
Ni	2.35691	1.91536
Cu	2.39119	1.98934
Zn	2.36493	2.08207

Table S2 ICP-OES results of β -MTC811, β -MT712 and β -MTC721

Sample	Measured atomic ration		
	Mn	Ti	Cu
β -MTC811	0.8	0.09	0.1
β -MTC712	0.7	0.08	0.2
β -MTC721	0.7	0.19	0.1

Table S3 Parameters for button cell batteries

Material	Cathodes' mass loading/mg	Electrolyte amount/ μ L	Radius/mm
β -MTC811	4.192	160	14
β -MTC721	4.360	160	14
β -MTC712	5.696	160	14