

Ca₂Nb₂O₇ as a Novel Open-framework Anode Material for Potassium-ion Batteries^①

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ABSTRACT Potassium-ion batteries (KIBs) are a promising alternative to Lithium-based energy storage systems owing to the low cost and rich abundance of potassium resources, but are facing challenges in designing low-cost hosts that can reversibly accommodate large-size K⁺ with fast diffusion kinetics. Herein, we report a novel 3D inorganic open framework of Ca₂Nb₂O₇ (CNO) as an anode for KIBs. The open framework structure affords interstitial vacancies available for storing K⁺ and allows a facile diffusion of K⁺, thus resulting in excellent structural stability and fast reaction kinetics. The CNO electrode delivers a reversible specific capacity of 65.3 and 52.2 mAh/g at 5 and 10 mA/g, respectively. Moreover, CNO exhibits excellent long-term cyclability with 92.53% capacity retention over 700 cycles at 10 mA/g. This will trigger more investigations into open-framework-based materials for stable and fast KIBs.

Keywords: potassium-ion batteries, inorganic-open-framework, long lifespan, kinetics;

DOI: 10.14102/j.cnki.0254-5861.2011-2862

1 INTRODUCTION

Lithium-ion batteries (LIBs) have dominated portable electronic devices market and have been widely used in electric vehicles^[1]. Despite great advances that have been made, LIBs still suffer from growing concerns for grid-scale energy storage due to the scarcity of lithium resources^[2]. It is highly desired to explore new battery chemistry based on earth-abundant elements, which can complement LIBs or serve as replacement for them. Recently, rechargeable potassium-ion batteries (KIBs) have attracted tremendous attentions as promising alternative energy storage systems due to the low cost and rich abundance of potassium

resources^[3, 4]. However, since the radius of K⁺ (1.38 Å) is much larger than that of Li⁺ (0.76 Å)^[5], electrode materials for KIBs often face the challenges of sluggish diffusion kinetics and large lattice strain upon K⁺ diffusion and insertion, causing huge voltage hysteresis and inferior structural stability. Therefore, developing stable hosts that can reversibly accommodate large K⁺ with rapid diffusion kinetics is extremely urgent for the development of KIBs.

To overcome the structural change and sluggish diffusion kinetics, materials with three-dimensional (3D) open frameworks which can facilitate K⁺ transport are considered as promising K⁺ hosts. Up to date, some Prussian blue analogues (PBAs) and polyanionic compounds with 3D open

Received 27 April 2020; accepted 18 June 2020

① Supported by the Natural Science Foundation of Fujian Province (No. 2018J01031), Open Project Program of the State Key Laboratory of Photocatalysis on Energy and Environment (No. SKLPEE-202013), Natural Science Foundation of Fujian Province (No. 2017J01412) and National Natural Science Foundation of China (No. 21506036)

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frameworks have been attempted as K⁺ hosts. For example, hexacyanometalates, known as PBAs, have been investigated as robust frameworks for cathode materials, providing large interstitial vacancies for storing K⁺[6-8]. Polyanion compounds^[9-11], such as KVOPO₄ and KVPO₄F exhibit small lattice volume shrinkages upon K⁺ extraction, offering high voltage plateaus up to 4 V vs K/K⁺. Despite their successes achieved in K⁺ cathode hosts, 3D open-framework structures functioned as K⁺ anode hosts are rare, with Ti-based polyanionic compounds largely making up this class. A typical example is KTi₂(PO₄)₃^[12], which is composed of two TiO₆ octahedra and three PO₄ tetrahedra units and can afford interstitial vacancies to accommodate K⁺. Similarly, KTiOPO₄ also possesses a 3D open-framework structure allowing fast K⁺ insertion, with a small volume increase of 9.5%^[13]. The advantages of open-framework structures, as well as the lack of suitable K⁺ anode hosts, stimulate the exploration of open-framework anode materials for KIBs.

Herein, we for the first time report an open framework of calcium-niobium oxide, namely Ca₂Nb₂O₇ (CNO), as an anode for KIBs. Due to the 3D framework providing large interstitial spaces for reversible K⁺ storage, the CNO exhibits high structural stability and thus excellent cyclability, with 92.53% capacity retention over 700 cycles at 10 mA/g. Also, CNO delivers a specific capacity of 65.3 and 52.2 mAh/g at 5 and 10 mA/g, respectively. These results show CNO could be a potential alternative for KIBs anode.

2 EXPERIMENTAL

2.1 Synthesis of CNO

In a typical synthesis, 1.128 mmol Nb₂O₅ and 2.256 mmol Ca(OH)₂ were added into 15 mL H₂O and homogenized by stirring for 30 min. The mixture was sealed in a 25 mL stainless-steel autoclave and heated at 200 °C for 72 h, followed by cooling to room temperature. The white powder of CNO was collected by centrifugation, washed with distilled water three times, and vacuum-dried at 80 °C for 12 h.

2.2 Electrochemical measurements

Electrochemical measurements were carried out with CR2032 coin-type devices. To prepare the CNO cathodes, CNO powder was thoroughly mixed with Super P carbon black and sodium carboxymethyl cellulose (CMC) with a weight ratio of 7:2:1 using deionized water as dispersing

solvent. The slurry was coated on Al foil and dried at 80 °C under vacuum for 12 h. The mass loading of the active material (CNO) is 1.5~1.7 mg/cm². All the batteries were assembled in an argon-filled glove-box (Vigor) (H₂O < 0.1 ppm, O₂ < 0.1 ppm). 5 M potassium bis(fluorosulfonyl)imide (KFSI) in diethylene glycol dimethyl ether (DEGDME) was used as electrolyte. K foil pressed on stainless steel spacer was used as counter electrode and separated from the CNO electrode using a glass microfiber filter (Whatman, Grade GF/F).

The cycling tests were performed at different current densities on battery testing systems (LANHE, CT2001A) with a voltage window from 0.01 V to 2.5 V. The specific capacities were calculated based on the mass of CNO. Cyclic voltammetry (CV) was tested on an electrochemical workstation (CHI600E) from 0.01 to 3.0 V at a scan rate of 0.1 mV/s. Galvanostatic intermittent titration technique (GITT) was carried out on a LANHE CT2001 instrument with current pulses of 30 min at a rate of 5 mA/g followed by a rest step for 3 h. Prior to the GITT test, all batteries were activated for one cycle by galvanostatic cycling at 5 mA/g. The K⁺ diffusion coefficients were calculated by the following formula:

$$D_{K^+} = \frac{4}{\pi\tau} \left(\frac{n_M V_M}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

Herein, τ is the duration time of the constant current pulse; V_M and n_M are the mole volume and mole number of active materials, respectively; S is the effective contact area of active materials; ΔE_s and ΔE_t are the change in the steady-state voltage and overall cell voltage upon applying a current pulse, respectively.

2.3 Material characterization

Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV powder X-ray diffractometers with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphological features of CNO were characterized by field emission scanning electron microscopy (SEM, SJU-8010). The microstructure of CNO was characterized by transmission electron microscope (TEM, HITACHI F20).

3 RESULTS AND DISCUSSION

CNO powder was obtained *via* a simple hydrothermal reaction. The XRD pattern and Rietveld refinement of CNO in Fig. 1a reveal its purity and cubic structure, with $a = b = c = 10.4445 \text{ \AA}$. Fig. 1b shows that the cubic CNO has a 3D

inorganic open-framework structure composed of NbO_6 and CaO_6 units, with 3D channels (3.7 Å) that could provide large interstitial vacancies to accommodate K^+ . The charge compensation can be balanced by the valence change of the Nb redox center. The SEM and TEM images (Fig. 1c and 1d)

indicate the CNO is composed of regular octahedral particles with size of 200~400 nm. The high-resolution TEM (HRTEM) image in Fig. 2e shows that the lattice fringes have an interplanar spacing of 2.6 Å, which agrees well with the spacing of the (400) crystal plane of CNO.

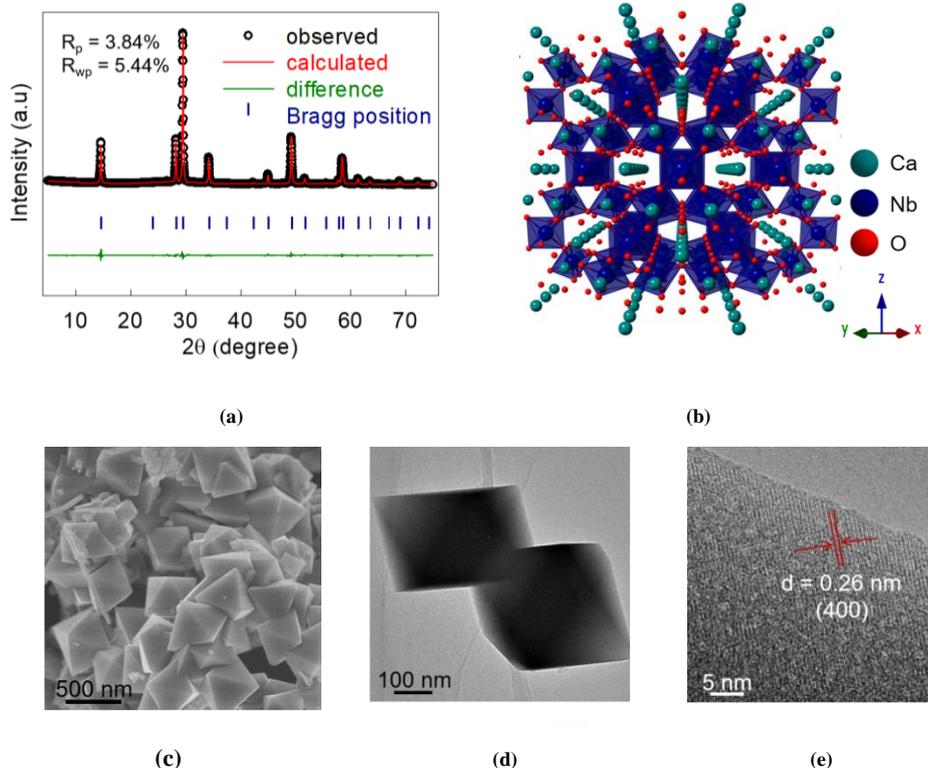


Fig. 1. (a) XRD and Rietveld refinement of CNO. (b) Projection view of CNO showing the inorganic open framework. (c) SEM, (d) TEM, and (e) HRTEM images of CNO

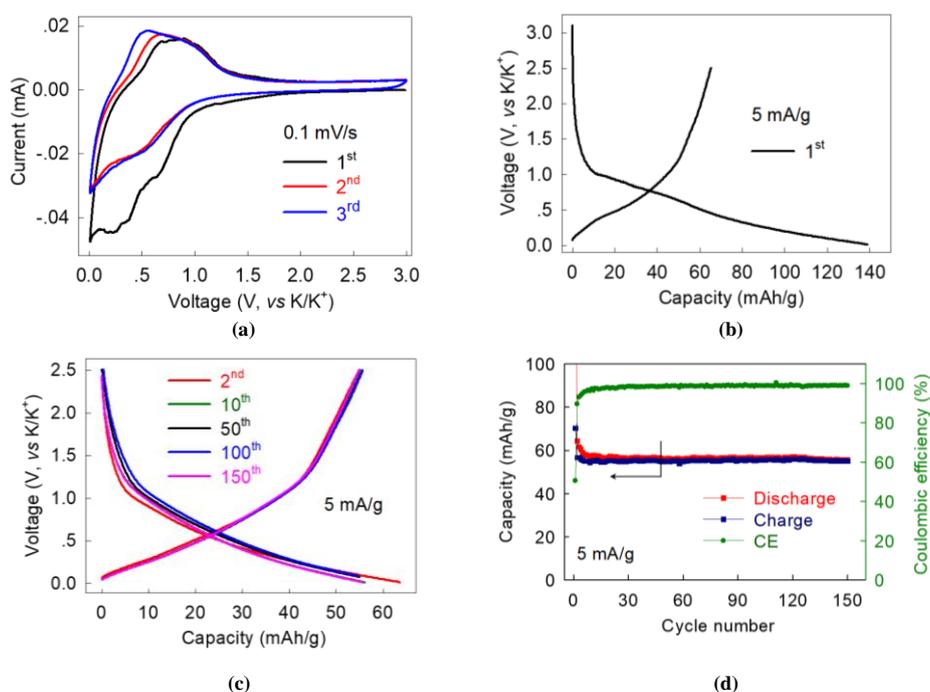


Fig. 2. (a) CV curves. Galvanostatic discharge and charge profiles of (b) the initial cycle and (c) the subsequent cycles at a current density of 5 mA/g. (d) Electrochemical cyclability of the CNO electrode at a current density of 5 mA/g

The electrochemical performances of CNO electrode were investigated in coin cells with K metal as counter electrode. Concentrated electrolyte (5 M KFSI-DEGDME) was used for high-efficient potassium plating/stripping. Fig. 2a presents CV curves of CNO anode at a scan rate of 0.1 mV/s within 0.01~3.0 V. Two cathodic peaks at 0.25 and 0.52 V appear in the first cycle and disappear in the following scan, which is ascribed to the K^+ insertion in CNO and the formation of solid electrolyte interface (SEI)^[14]. During the following cycles, anodic peak at 0.68 V and cathodic peak at 0.51 V are observed, which can be attributed to the (de)insertion of K^+ . The small voltage polarization indicates fast reaction kinetics. Moreover, the overlap of the following CV curves indicates high stability of K^+ (de)insertion chemistry. Fig. 2b shows the galvanostatic charge-discharge profiles of CNO anode between 0.01 and 2.5 V at a current density of 5 mA/g. A tiny voltage hysteresis is observed, which is in good accordance with CV results. The CNO electrode achieves an initial specific discharge capacity of 139 mAh/g and a specific charge capacity of 65.3 mAh/g. This suggests that ~ 0.9 K^+ ion per unit formula can be reversibly extracted from CNO, which is close to one-electron transfer reaction (theoretical capacity 71 mAh/g). The low initial Coulombic efficiency (CE) of 46.98% can be mainly attributed to the irreversible formation of the SEI^[15]. The following cycles are shown in Fig. 2c, in which the

charge and discharge plateaus of CNO are still clearly visible. A high capacity retention of 85.14% is achieved after 150 cycles with a CE approaching 100% (Fig. 2d), suggesting the high stability of CNO for K^+ ion insertion.

Furthermore, the long-term stability test also reveals the excellent structural stability of CNO, as shown in Fig. 3a and 3b. The CNO anode delivers an initial capacity of 46.6 mAh/g at 10 mA/g (0.14 C, 1 C = 71 mA/g), and shows a gradual increase in the capacity, achieving a maximum value of 52.2 mAh/g after 242 cycles. This phenomenon may be ascribed to the continuous electrolyte saturating, which has been observed in previous reports^[12]. After 700 cycles, the capacity is maintained at 48.3 mAh/g, corresponding to a high capacity retention of 92.53% with capacity decay of 0.016% per cycle. This cyclability at low current density is superior to most, if not all, reported anode materials for KIBs^[3, 11-13, 16-21]. The excellent cyclability is mainly due to the structural robustness of 3D inorganic open framework. In addition, the CNO electrode also exhibits good rate capability. As shown in Fig. 3c, CNO delivers reversible capacities of 53.8, 51.6, 46.3, 39, 33.4 mAh/g at 5, 10, 20, 50, 100 mA/g, respectively. Moreover, the electrode achieves a reversible capacity of 57.5 mAh/g when the current density is recovered to 5 mA/g, which represents excellent structural stability and fast K^+ -insertion kinetics.

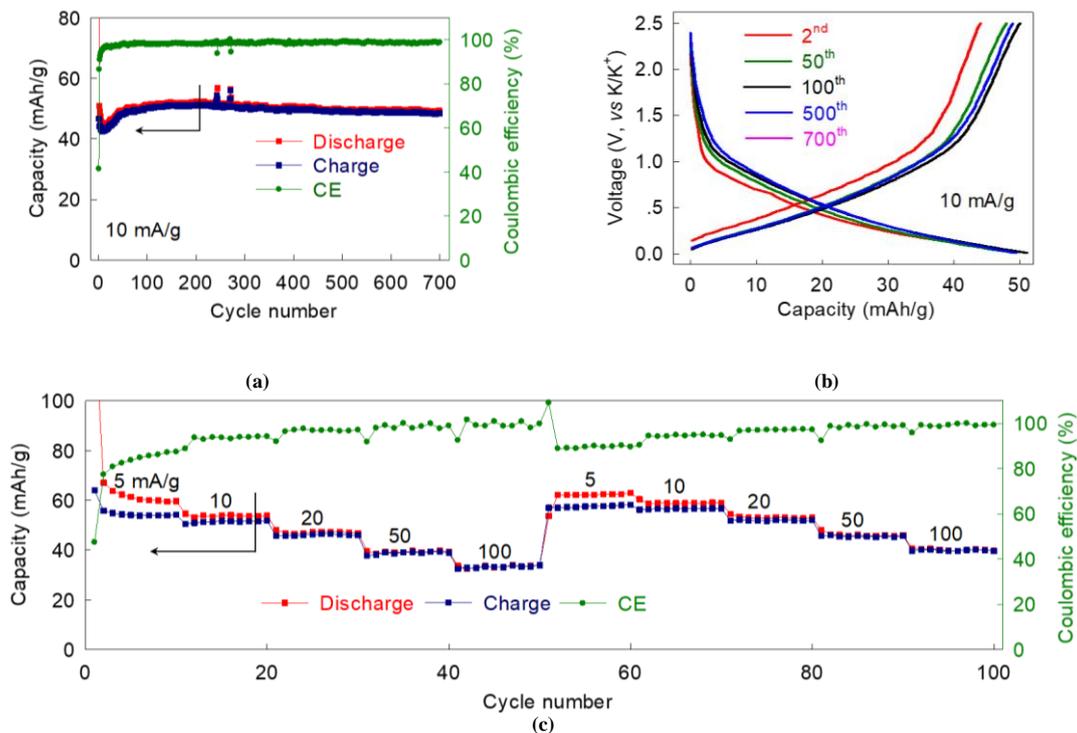


Fig. 3. (a) Long-term cyclability of the CNO anode at a current density of 10 mA/g and (b) corresponding voltage profiles. (c) Rate capability

To gain further insight into the electrochemical kinetics, GITT test was performed to examine the diffusion coefficients of K^+ (D_{K^+}). As shown in Fig. 4, the CNO displays an average D_{K^+} of $1.2 \times 10^{-11} \text{ cm}^2/\text{s}$, which is comparable to the D_{K^+} in graphite ($\sim 10^{-13} \text{ cm}^2/\text{s}$)^[22, 23] and G@C@SnO₂ anode ($10^{-15} \sim 10^{-14} \text{ cm}^2/\text{s}$)^[24], and even higher

than the diffusion coefficient of Li^+ in LiFePO₄ ($10^{-15} \sim 10^{-14} \text{ cm}^2/\text{s}$)^[25], indicating fast K^+ -insertion kinetics. Such high diffusion coefficients in CNO are ascribed to its 3D inorganic open framework structure, and make it a promising anode material for KIBs.

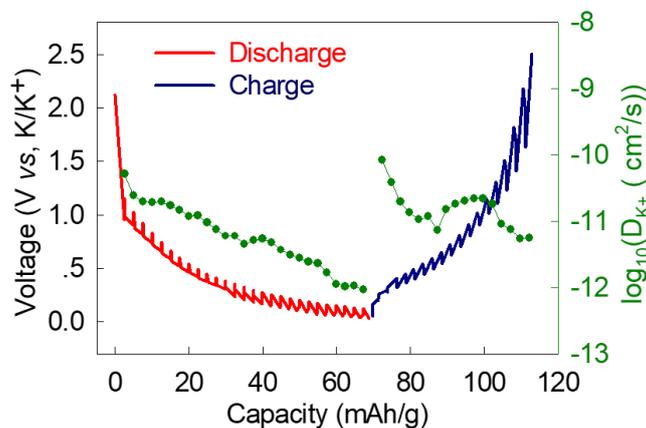


Fig. 4. GITT profiles and calculated K^+ diffusion coefficients of CNO

4 CONCLUSION

In conclusion, a novel 3D inorganic open framework of calcium-niobium oxide as an anode for KIBs is reported for the first time. The open framework structure provides large interstitial spaces for reversible K^+ storage and allows facile diffusion of K^+ , thus leading to excellent structural stability

and fast reaction kinetics. The CNO electrode delivers a reversible capacity of 65.3 mA/g, a moderate rate capability (33.4 mA/g at a current density of 200 mA/g), and excellent cycle stability (92.53% capacity retention over 700 cycles). These results highlight the CNO electrode as a promising anode for KIBs and will trigger further researches on the 3D open-framework electrode materials.

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