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Nanostructured potassium–organic framework as an effective anode for potassium-ion batteries with a long cycle life†

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Finding new organic materials to address several issues (e.g. capacity, stability, and cycle life) in organic potassium-ion batteries (OPIBs) is very important and highly desirable. Here, to directly investigate the redox reaction of organic pyridine dicarboxylate in OPIBs and to avoid the interference from the redox-active metal ions, a non-redox-metal potassium metal–organic framework (K-MOF), [C7H3KNO4]n, based on pyridine-2,6-dicarboxylic acid (H2PDA), has been successfully synthesized and applied as a promising organic anode for long-cycle life PIBs. The crystal structure of [C7H3KNO4]n was confirmed by single-crystal X-ray diffraction analysis and FT-IR spectra. Moreover, the potassium-storage mechanism of organic pyridine dicarboxylate ligand was revealed by ex situ FT-IR/XRD characterization and theoretical calculations. The as-synthesized K-MOF resulted in a unique and reversible three-step redox reaction, exhibited superior electrochemical performance with the aid of N–K/O–K coordination bonds, and showed a high average specific capacity of 115 mA h g−1 at 100 mA g−1 for 300 cycles with the capacity retention of 92%.

Introduction

Owing to the fast kinetics of K+ cation, the abundance of potassium (~2.09 wt%) in the Earth’s crust,1−3 and the nature of organic materials (i.e., contrivable structure, flexibility, and enough void room of organic materials to accommodate the large radius of K+ cation (1.38 Å)),4−6 organic potassium-ion batteries (OPIBs) have been widely considered as the next-generation battery system for stationary energy storage.7−14 In the previous research studies, many organic materials, such as the organic cathodes based on CuTCNQ,15 quinones,16 Prussian blue analogs,13,17,18 and dianhydrides,19 have been demonstrated as cathodes in OPIBs. However, the excellent organic materials as anodes in OPIBs are still limited at present.20−24 More importantly, the electrochemical performance of organic anodes in OPIBs still needs to be further improved, especially for the long-cycle performance.

Metal–organic frameworks, developed through the coordination bonds between organic ligands and metal ions or clusters,25 have been employed as promising electrode materials for lithium-ion batteries because of their structural diversity and flexibility, high specific capacity, and the enhanced electrochemical performance from the combination of metal ions and organic ligands.26 The metal–organic frameworks based on the “universal ligand” pyridine-2,6-dicarboxylic acid (H2PDA) and its derivatives have been extensively applied as promising electrode materials for lithium-ion batteries with relatively high specific capacity (i.e., [Li6(pda)3]·2EtOH and [Co1.3(L(H2O))6])26,27 However, to date, none of the metal–organic frameworks containing the functional ligand pyridine-2,6-dicarboxylic acid has been employed as anodes in OPIBs.20 Such a gap strongly encourages us to conduct our research in this direction.

To directly investigate the redox reaction of the organic pyridine dicarboxylate ligand in OPIBs and to avoid the interference from the redox-active metal ions (such as Co, Ni, Cu and Fe ions), a pristine potassium metal–organic framework (K-MOF) as a non-redox-metal-involved MOF provides a better option and would help us to directly study the detailed potassium storage mechanism of pristine organic ligands in OPIBs.

In this study, a novel K-MOF ([C7H3KNO4]n), developed from the organic ligand pyridine-2,6-dicarboxylic acid (H2PDA)

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and K⁺, was employed as an advanced anode in OPIBs. The as-fabricated batteries showed a high specific capacity of 163 mA h g⁻¹ and maintained a high average specific capacity of 115 mA h g⁻¹ (with a capacity retention of 92%) at 100 mA g⁻¹ for 300 cycles. Such high performance might be due to the stable bonds of N–K and O–K in the K-MOF, which allows the K⁺ ions to easily intercalate into or de-intercalate from the inner space of the K-MOF.

Results and discussion

The chemical structure of the K-MOF ([C₇H₃KNO₄]ₙ) was confirmed by single-crystal X-ray diffraction analysis (SCXRD) and FT-IR spectra. The zigzag chain structure of the colorless crystals of [C₇H₃KNO₄]ₙ is shown in Fig. 1. In [C₇H₃KNO₄]ₙ, each C₇H₃KNO₄ unit contains five K ions through five O–K bonds and one N–K bond (Fig. 1a), where each K ion is seven-coordinated with two O atoms and one N atom from one organic ligand, and four O atoms from four other organic ligands (Fig. 1b). These K ions are connected with O atoms in up-and-down modes to generate a 1D zigzag chain. Then, these chains are further linked together by K ions and C₇H₃NO₄⁻ anions to give a 2D layered structure and 3D architectures (Fig. 1c and d). The corresponding fractional atomic coordination and equivalent isotropic displacement parameters are shown in Table S1,† which possess the monoclinic space group of I2/a. Meanwhile, in the FT-IR spectra (Fig. S1a†), the new emerging bands of O–K/N–K vibrations locate at 457/501 cm⁻¹, respectively, and the vibrations at ~1373 cm⁻¹ and 1640 cm⁻¹ belong to the ν(COO⁻) vibrations.²⁴ Correspondingly, in comparison, the band of C=O vibration at 1700 cm⁻¹ in H₂PDA disappeared, and the bands at 420 and 648 cm⁻¹ (belonging to the vibrations of the pyridine ring in H₂PDA) were blue-shifted (446 and 699 cm⁻¹, respectively). Furthermore, [C₇H₃KNO₄]ₙ has a higher thermal decomposition temperature (455 °C) than H₂PDA (Fig. S1b†). The powder X-ray diffraction (XRD) peaks of [C₇H₃KNO₄]ₙ match well with the calculated pattern (Fig. S2†). Additionally, as observed from the SEM images (Fig. 3a), nanostructured [C₇H₃KNO₄]ₙ exhibits a relatively uniform shape of rectangular blocks with a mean size of 100 nm.

The potassium storage performance of [C₇H₃KNO₄]ₙ is carried out between 0.1 and 2.0 V by using CR 2032 coin cells. The selected galvanostatic discharge–charge curves of [C₇H₃KNO₄]ₙ are shown in Fig. 2a, which show three pairs of discharge/charge potential plateaus. The low initial coulombic efficiency might be mainly caused by the neat super P (Fig. S3†) and the sufficient formation of SEI layer.²⁰,²³ After the 1st cycle, the discharge/charge potential plateaus remain highly consistent, and the reversible capacities (~159 mA h g⁻¹) are very stable. The CV curves of [C₇H₃KNO₄]ₙ are investigated at a scan rate of 0.1 mV s⁻¹, as shown in Fig. 2b. Interestingly, during the 1st K⁺ cation intercalation process, [C₇H₃KNO₄]ₙ showed a three-step reduction behavior with the reduction potentials of ~0.74 V, 0.48 V, and 0.26 V, respectively. Gradually, during the 2nd intercalation/de-intercalation process, [C₇H₃KNO₄]ₙ shows three clear and stable redox couples with the reversible anodic/cathodic couples located at ~0.22/0.66 V, ~0.48/0.74 V and ~0.82/1.08 V, respectively, which are consistent with the three pairs of discharge/charge potential plateaus. These peaks show a strong ligand coordination of K⁺ cations with [C₇H₃NO₄]⁻ anions during the potassiation and de-potassiation processes. Additionally, the potential at 0.48 V in the 1st anodic scan is also attributed to the formation of the solid–electrolyte interface (SEI). Moreover, as expected, [C₇H₃KNO₄]ₙ shows a good rate performance in PBs (Fig. 2c) with the sequentially changed current densities from 10 to 1000 mA g⁻¹. At current rates of 10/20/50/100/200/500/1000 mA g⁻¹, the corresponding rate capacities are 155/142/127/108/79/44/16 mA h g⁻¹, respectively. The corresponding contribution of the super P (30 wt%) is in the range of 56–9 mA h g⁻¹ from 10 to 1000 mA g⁻¹ (Fig. S4†).

![Fig. 1](image1.png)

Fig. 1. The zigzag chain structure of the colorless transparent crystal [C₇H₃KNO₄]ₙ. (a–b) Coordination mode of [C₇H₃KNO₄]ₙ (inset: the picture of a typical single crystal). (c) 2D layered structure of the K-MOF. Inset: 1D chain structure connected by O atoms of the carboxylate group. (d) Schematic drawing of the 3D K-MOF.

![Fig. 2](image2.png)

Fig. 2. The electrochemical performance of [C₇H₃KNO₄]ₙ anode. (a) Selected discharge–charge curves at 10 mA g⁻¹; (b) CV curves at the scan rate of 0.1 mV s⁻¹; (c) rate performance; and (d) long-cycle profile at 50 mA g⁻¹.
Furthermore, \([\text{C}_7\text{H}_3\text{KNO}_4]_n\) shows a good long-cycle profile at the current density of 50 mA g\(^{-1}\) when an average capacity of 123 mA h g\(^{-1}\) for 150 cycles with the capacity retention of 90\% (Fig. 2d) is achieved.

To dramatically enhance the electron/ion-transporting kinetics of \([\text{C}_7\text{H}_3\text{KNO}_4]_n\), highly conductive CNTs are used as the host matrix to \textit{in situ} composite with the nanoparticles of \([\text{C}_7\text{H}_3\text{KNO}_4]_n\). After \textit{in situ} mixing, \([\text{C}_7\text{H}_3\text{KNO}_4]_n@\text{CNTs}\) show high uniformity and the CNTs uniformly disperse into the \([\text{C}_7\text{H}_3\text{KNO}_4]_n\) nanoparticles, confirmed by the SEM image (Fig. 3b).

Meanwhile, the \textit{in situ} combination with CNTs does not significantly alter the electrochemical behavior of \([\text{C}_7\text{H}_3\text{KNO}_4]_n\) (Fig. S4†), and at the same time, the charge-transfer impedance (Fig. S4b†) decreases. Moreover, as expected, the three-step redox reaction of \([\text{C}_7\text{H}_3\text{KNO}_4]_n@\text{CNTs}\) is more reversible and stable (Fig. 4a), and the three-step discharge/charge plateaus are evident and eye-catching under different current rates (Fig. 4b). Additionally, \([\text{C}_7\text{H}_3\text{KNO}_4]_n@\text{CNTs}\) show excellent electrochemical performance, including high rate abilities and large capacities as well as superior long-cycling performances. As shown in Fig. 4c, the satisfactory rate capacities of 163/144/128/113/100/90/80/60 mA h g\(^{-1}\) are obtained at the current rates of 10/20/50/100/200/500/1000/2000 mA g\(^{-1}\), respectively. At the current density of 100 mA g\(^{-1}\), it gains an average specific capacity of 115 mA h g\(^{-1}\) within 300 cycles with the capacity retention of 92\% (Fig. 3d), which is comparable to the recently reported anode materials.\(^{24,28,29}\) As shown in Fig. 4e, \([\text{C}_7\text{H}_3\text{KNO}_4]_n@\text{CNTs}\) show an average specific capacity of 40 mA h g\(^{-1}\) for 1500 cycles even at a high current density of 1000 mA g\(^{-1}\). The capacity lost in the first few cycles was caused by the battery activation.\(^{2,3,29}\)

To understand the potassium storage mechanism of \([\text{C}_7\text{H}_3\text{KNO}_4]_n\) between 0.1 V and 2.0 V, the \textit{ex situ} FT-IR and XRD measurements were carried out (Fig. 5). During the potassiation process (point A–E), the non-benzene C\(^\equiv\)C vibration at \(\sim 1654 \text{ cm}^{-1}\), which is weak in the pristine (point A), gradually becomes stronger, while in the following depotassiation process (point E–I), this peak gradually becomes weaker. Meanwhile, the intensity fluctuation of non-benzene C\(^\equiv\)C vibration is related to the formation of C–O/C\(^\equiv\)O bonds with the intercalation/de-intercalation of K\(^+\) cations during the discharge/charge processes, respectively, which is similar to the previous reports about K-storage mechanism for potassium dicarboxylate derivatives.\(^{20,21,30}\) In contrast, in both the potassiation and depotassiation processes (point A–I), the pan-fre-
quency peak of $\delta_{\text{C-H}}$ vibration, located at 1805, 1776 and 1712 cm$^{-1}$, and the out-of-plane C–H deformation (700 cm$^{-1}$) showed unique and complex changes. They first appear and then vanish (Fig. 5b), consisting of the previous 3-step CVs. This result could be due to the change of crystal symmetry caused by the intercalation/de-intercalation of K$^+$ with the coordination bonds of N–K/O–K in [C$_7$H$_3$KNO$_4$]$_n$. Moreover, the peak at 600 cm$^{-1}$ belongs to the components of the SEI layer,$^{24}$ and the pyridine coordination bond (1450 cm$^{-1}$)$^{31}$ remains almost unchanged during the battery operation. To further realize the change of crystal symmetry, the ex situ XRD patterns at different potentials are employed. As shown in the ex situ XRD pattern (Fig. 5c), with the intercalation/de-intercalation of K$^+$ cations, there are no appreciable changes observed in the XRD patterns except for the complicated change of crystallographic-preferred orientation (point A–I). More importantly, after the intercalation and then the de-intercalation of K$^+$ cations, the crystallographic-preferred orientation of [C$_7$H$_3$KNO$_4$]$_n$ (point I) is different from the pristine (point A).

Additionally, the CASTEP calculations show that the inserted K$^+$ cations (denoted as K$^\prime$) are stored at (1/2, 1/2, 0) and (1/2, 1/2, 1/2), which locate at the interface of each different repeating unit layer of [C$_7$H$_3$KNO$_4$]$_n$ when one K$^+$ cation is intercalated into one repeating unit of [C$_7$H$_3$KNO$_4$]$_n$ to form [C$_7$H$_3$K$_2$NO$_4$]$_n$. The zigzag chain structure of [C$_7$H$_3$K$_2$NO$_4$]$_n$ and the corresponding calculated [C$_7$H$_3$K$_2$NO$_4$]$_n$ are shown in Fig. 6a and b, respectively. In [C$_7$H$_3$K$_2$NO$_4$]$_n$, each C$_7$H$_3$K$_2$NO$_4$ part includes three O–K bonds and two O–K$^\prime$ bonds (Fig. 5b), and each K ion is five-coordinated with two O atoms and one N atom from one organic ligand, and two O atoms from two other organic ligands. Meanwhile, each K$^\prime$ ion is two-coordinated with two O atoms from two organic ligands. Therefore, each C$_7$H$_3$K$_2$NO$_4$ unit contains one K atom and one inserted K$^\prime$ atom. Furthermore, the experimental and calculated lattice parameters for the conventional cell of [C$_7$H$_3$KNO$_4$]$_n$ and [C$_7$H$_3$K$_2$NO$_4$]$_n$ are listed in Table S2,$^\dagger$ respectively. Expectedly, with the potassiation of [C$_7$H$_3$KNO$_4$]$_n$, the initial cell volume of [C$_7$H$_3$K$_2$NO$_4$]$_n$ (cal. 1250.248 Å$^3$) is expanded compared to [C$_7$H$_3$KNO$_4$]$_n$ (739.7 Å$^3$) for the intercalation of large K$^+$ cations. In the calculated potassiated [C$_7$H$_3$K$_2$NO$_4$]$_n$ cell, the distance between two neighboring K$^+$ cations (K–K) is 8.472 Å (4.236 Å for K–K$^\prime$), which is higher than the distance between the original K$^+$ cations (4.629 Å for K–K$^\prime$).

According to the above results, the redox reaction mechanism of [C$_7$H$_3$KNO$_4$]$_n$ is concluded as follows:

\begin{equation}
\text{Discharge: } [\text{C}_7\text{H}_3\text{KNO}_4]_n + n\text{K}^+ + ne^- \\
\rightarrow \text{K}^n \cdot [\text{C}_7\text{H}_3\text{KNO}_4]_n^{n-}. 
\end{equation}

\begin{equation}
\text{Recharge: } \text{K}^n \cdot [\text{C}_7\text{H}_3\text{KNO}_4]_n^{n-} - n\text{K}^+ - ne^- \\
\rightarrow [\text{C}_7\text{H}_3\text{KNO}_4]_n.
\end{equation}

### Conclusions

In summary, to directly investigate the redox reaction of organic pyridine dicarboxylate ligand in OPIBs and to exclude the interference from the redox-active metal ions, a K-MOF ([C$_7$H$_3$KNO$_4$]$_n$) based on H$_2$PDA was synthesized and initially exploited as an advanced organic anode with a long cycle life in OPIBs. The potassium-storage mechanism of organic pyridine dicarboxylate ligand was revealed by ex situ FT-IR/XRD characterization and theoretical calculations. The as-synthesized [C$_7$H$_3$KNO$_4$]$_n$ resulted in a unique and reversible three-step redox reaction and showed excellent rate capacities and superior long-cycle capacities with the assistance of abundant N–K/O–K coordination bonds. This work paves a promising way to employ K-MOFs as efficient electrode materials for OPIBs.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references