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Copper Porphyrin as a Stable Cathode for High-Performance Rechargeable Potassium Organic Batteries

Shenshen Lv⁺,^[a] Jingjun Yuan⁺,^[a] Zhi Chen,^[b, d] Ping Gao,^{*[a]} Hongbo Shu,^[a] Xiukang Yang,^[a] Enhui Liu,^{*[a]} Songting Tan,^[a] Mario Ruben,^[b] Zhirong Zhao-Karger,^[b, c] and Maximilian Fichtner^[b, c]

Rechargeable potassium-ion batteries (KIBs) are promising alternatives to lithium-ion batteries for large-scale electrochemical energy-storage applications because of the abundance and low cost of potassium. However, the development of KIBs is hampered by the lack of stable and high-capacity cathode materials. Herein, a functionalized porphyrin complex, [5,15-bis-(ethynyl)-10,20-diphenylporphinato]copper(II) (CuDEPP), was proposed as a new cathode for rechargeable potassium batteries. Spectroscopy and molecular simulation studies were used

Introduction

With the rapid development of electronic devices, electric vehicles, and large-scale electrochemical energy storage (EES), electrode materials with high energy density, low-cost, and reliable safety are crucial.^[1-4] Lithium ion batteries (LIBs), with the merits of excellent power and energy density, have been investigated extensively and utilized widely for various applica-

[a]	S. Lv, ⁺ J. Yuan, ⁺ Dr. P. Gao, Dr. H. Shu, Dr. X. Yang, Prof. E. Liu, Prof. S. Tan Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education Key laboratory for Green Organic Synthesis and Application of Hunan Prov- ince College of Chemistry Xiangtan University 411105, Xiangtan (P.R. China) E-mail: ping.gao@xtu.edu.cn liuenhui99@sina.com
[b]	Dr. Z. Chen, Prof. M. Ruben, Dr. Z. Zhao-Karger, Prof. M. Fichtner Institute of Nanotechnology Karlsruhe Institute of Technology P.O. Box 3640, 76021 Karlsruhe (Germany)
[c]	Dr. Z. Zhao-Karger, Prof. M. Fichtner Helmholtz Institute Ulm (HIU) Helmholtzstrasse 11, 89081 Ulm (Germany)
[d]	Dr. Z. Chen International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education Institute of Microscale Optoelectronics Shenzhen University Shenzhen 518060 (P.R. China)
[+]	These authors contributed equally to this work.
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to show that both PF_6^- and K⁺ interact with the porphyrin macrocycle to allow a four-electron transfer. In addition, the electrochemical polymerization of the ethynyl functional groups in CuDEPP resulted in the self-stabilization of the cathode, which was highly stable during cycling. This unique charge storage mechanism enabled CuDEPP to provide a capacity of 181 mAhg⁻¹ with an average potential of 2.8 V (vs. K⁺/K). These findings could open a pathway towards the design of new stable organic electrodes for KIBs.

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tions.^[5–8] However, limited lithium resources and their uneven geographical distribution largely hinder the further development of LIBs in the case of large-scale energy-storage applications.^[9,10] Researchers are, therefore, devoting substantial efforts to investigate more sustainable alternative EESs. Particular attention is paid to the analogs of LIBs, sodium-ion batteries (SIBs)^[11] and potassium-ion batteries (KIBs),^[12-16] because of the abundance of sodium and potassium resources in the Earth's crust. Potassium possesses a lower standard hydrogen potential (-2.92 V vs. standard hydrogen electrode, SHE) than sodium (-2.71 V vs. SHE), which leads to the higher energy density of KIBs.^[17-20] Additionally, fast charge/discharge can be expected in KIBs because of the relatively weaker Lewis acidity of K⁺ compared to Li⁺ and Na⁺, which is beneficial for ion mobility in the liquid electrolyte, at the electrode-electrolyte interface, and in solids.^[21,22] The large ionic radius of K^+ (1.38 vs. 0.76 Å for Li⁺ and 1.02 Å for Na⁺) increases the kinetics in some host electrodes significantly; therefore, the development of suitable insertion materials to accommodate K⁺ is crucial.

The reversible intercalation of K ions in graphitic materials is a thermodynamically favored reaction through the formation of KC₈,^[13] and various carbonaceous materials (i.e., graphite, hard carbon, and soft carbon) have been investigated as a host for the anode.^[23-25] Capacities near the theoretical value (279 mAh g⁻¹) and a potential of approximately 0.2 V versus K⁺/K were found. Other high-capacity anode materials that include metals (i.e., Sn, Bi, and Sb)^[26,27] and metal oxides (i.e., MoO₃ and K₂Ti₄O₉)^[28,29] have been proposed. In addition, organic materials (i.e., dipotassium terephthalate and potassium 1,1'-biphenyl-4,4'-dicarboxylate) have been explored as anodes for KIBs.^[30,31] However, the identification of suitable cathode materials remains a challenge for the realization of KIBs be-

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cause of the limited charge-storage sites and large K⁺ radius in the host cathode material. Inorganic layered materials K_xMO₂ $(M = Mn, Co, Fe, Ti)^{[32-35]}$ and polyanionic compounds^[36, 37] have been considered as potential cathode materials for KIBs and are supposed to have a similar charge-storage mechanism as in LIBs and SIBs. However, these inorganic cathodes suffer from low voltage, low capacities, and poor cyclability, which indicates the intrinsically unfavorable capability of K-ion insertion. Prussian blue and its analogues have been demonstrated to be promising cathode materials for KIBs in terms of operation potential and cycling stability, but their reversible capacities need to be further increased.[38,39] In contrast to the rigid structure that results from the strong ionic bonding in inorganic compounds, organic materials consist of discrete molecules held together by much weaker intermolecular interactions, which renders them flexible. As a result of their tunable theoretical capacities, flexible structures, environmental friendliness, and low production cost,^[40-43] organic cathode materials could be a favorable option as host materials to accommodate K⁺. However, as a result of the high solubility of organic active materials in liquid electrolytes, only a few organic materials have been investigated as a cathode for KIBs to date.[41,42] The design of insoluble polymers and their composites are effective strategies to alleviate the dissolution of active materials. In addition, the intrinsic low electronic conductivity of the polymer electrode materials used commonly remains a roadblock to achieve a high rate performance of organic battery systems.

Recently, porphyrin-based redox active materials have emerged as a new class of organic electrodes for ultrafast electrochemical energy storage.[44,45] As a result of their unique properties of electron transfer and molecular self-assembly, porphyrin-derived synthetic strategies can address both issues of solubility and electric conductivity synergistically. Porphyrins with appropriate functional groups have the tendency to selfassemble and, thereby, form covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) with a low solubility in organic solvents. $^{[46,47]}$ As a result of the extended $\pi\text{-}$ conjugated structure, electrons can be taken up or released easily by expanding or shrinking the aromatic or antiaromatic systems on the macrocycles, which enables fast redox processes. Moreover, porphyrin-derived materials have unique merits such as insolubility and high electronic conductivity, which render them promising candidates as high-performance organic cathode materials. It was proven that porphyrins could serve as bipolar organic electrodes by donating or accepting electrons at its macrocyclic core to realize multiple electron transfer to provide both high energy and high power density within one system.^[44,48] Recently, porphyrin-based COF and MOF materials were investigated for EES,^[46, 47] which suggests new organic compounds for high-performance energy storage. Previous studies showed that functionalized porphyrin molecules can undergo electrochemical polymerization through the ethynyl groups during the charging process to connect the porphyrin units into an extended π -conjugated framework with a high electronic conductivity and low solubility. This material demonstrated both high specific power density (29 kW kg⁻¹) and energy density (345 Wh kg⁻¹) even after a long cycling life in LIBs. These interesting results motivated us to broaden the application of functionalized porphyrin complexes in energy-storage systems and to better understand the charge storage mechanism of porphyrin-based systems. In this work, we explore the charge storage of both potassium cations and anions in [5,15-bis(ethynyl)-10,20-diphenylporphinato]copper(II) (CuDEPP) and investigate the reaction mechanism during the electrochemical process. Ex situ IR spectroscopy, Xray photoelectron spectroscopy (XPS), powder XRD, and DFT were applied to elucidate the sequential structural evolution of CuDEPP during the electrochemical processes to probe the potassium cations and counter anions dynamics at the porphyrin redox center and, thereby, to investigate the variation of CuDEPP and its multielectron transfer capability.

Results and Discussion

Details of the synthesis and chemical characterization of CuDEPP are provided in the Experimental Section in the Supporting Information. We used SEM to reveal that the obtained CuDEPP solids were rod-shaped crystals. Elemental mapping obtained by using energy-dispersive X-ray spectroscopy (EDX) indicated that N and Cu were distributed homogeneously in the CuDEPP particles (Figure S2 in the Supporting Information). CuDEPP showed very limited solubility in common solvents, such as propylene carbonate (PC) and dimethyl carbonate (DMC), and no color change was seen if CuDEPP was placed in these solvents, a prerequisite for a stable electrode material in liquid-electrolyte-based rechargeable batteries. The electrochemical redox chemistry of the CuDEPP electrode material is supposed to be a reversible oxidation and reduction of the aromatic porphyrins (18 π) with the formation of a dicationic species (16 π) and a dianionic species (20 π) because of the bipolar properties of the porphyrin molecule, in which in total four electrons can be transferred easily in the highly conjugated porphyrin macrocycle.[44,48] As a result of the bipolar redoxactive properties, the electrochemical processes of CuDEPP in a KIB are proposed in Scheme 1a. Both cations and anions contribute to the charge storage during the charge and discharge processes. To study the reaction mechanism of CuDEPP in KIBs systematically, half-cells and full cells were designed. In a half-cell configuration (Scheme 1 b), the CuDEPP cathode was coupled with a K metal negative electrode, and in a full cell, a graphene anode was used. KPF₆- and KTFSI-based (TFSI=trifluoromethanesulfonimide) electrolytes were used to fully demonstrate the charge-storage capability.

A charge capacity of 2474 mAh g⁻¹ and a discharge capacity of 424 mAh g⁻¹ were obtained in the first cycle (Figure S3 a in the Supporting Information); both capacities were higher than the theoretical value of 187 mAh g⁻¹ based on a four-electron transfer. The higher capacity and the remarkable capacity difference between the first and the following cycles can be attributed to the electropolymerization of CuDEPP through the ethynyl group in an initial formation step, to the oxidation of CuDEPP in the formation of CuDEPP-16 π species, and the formation of cathodic electrolyte interface in the first cycle, which will be discussed below. A flat voltage plateau at approximateFull Papers doi.org/10.1002/cssc.202000425



Scheme 1. Bipolar redox activity of the copper porphyrin complex in KIBs. Schematic illustrations of (a) a K/KPF₆/CuDEPP half-cell and (b) a graphene/KPF₆/CuDEPP full cell during the discharge process.

ly 4.2 V (vs. K⁺/K) was observed in the first charging process, which is consistent with the irreversible feature of the cyclic voltammetry (CV) curve (Figure S3 b in the Supporting Information). After the initial cycle(s), highly reversible charge and discharge processes were observed. Capacity contributed by acetylene black can be ignored because a discharge capacity of

only 4 mAhg⁻¹ was observed with a respective electrode under the same cycling conditions (Figure S4 in the Supporting Information). No well-defined voltage plateau was displayed in the charge-discharge profiles for the CuDEPP electrode in KIB, which may be attributed to the distinct redox mechanism, in which electrons are transferred successively into the unoccupied molecular orbital. Similar sloping curve behavior is often observed in organic electrodes with a pseudocapacitive contribution.[49] In a voltage range of 1.7-4.5 V (vs. K⁺/K), the CuDEPP cathode delivered a discharge capacity of 181 mAh g⁻¹ in the second cycle, at a current density of 0.2 Ag^{-1} , which is close to the theoretical capacity of 187 mAh g⁻¹ based on four-electron transfer (Figure S3 in the Supporting Information). With this energy, the cell can easily light 26 yellow light-emitting diodes (LEDs) in series (Figure S5 in the Supporting Information).

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The cycling performance of the CuDEPP cathode was examined at a current density of 0.3 Ag^{-1} in a potential window of 1.7-4.5 V (vs. K⁺/K) in a half-cell configuration (Figure 1 a). Gradually, the discharge capacity became stable after three initial cycles and

was maintained at 147 mAh g^{-1} in the fourth cycle. After 300 cycles, it still displayed a reversible capacity of 128 mAh g⁻¹ with a capacity retention of 87%, which suggests a good cycling stability. Notably, a high energy density of 408 Wh kg⁻¹ (based on the active material) was obtained at 0.3 A g⁻¹ (Figure 1 a), which corresponds to a power density of



Figure 1. Electrochemical performance of the K/KPF₆/CuDEPP cell. (a) Cycling performance of the cell in terms of specific capacity and energy density at 0.3 A g⁻¹. (b) Galvanostatic charge and discharge curves in the 50th, 100th, 200th, and 300th cycles. (c) Discharge capacities and corresponding coulombic efficiencies at various current densities from 0.1 to 1 A g⁻¹. (d) Selected discharge profiles at different current densities.

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859 W kg⁻¹, with an energy density retention of 87% within 300 cycles, indicating that both the specific capacity and discharge voltage can be well retained upon cycling. Selected charge-discharge curves of the CuDEPP cathode in different cycles (50th, 100th, 200th, 300th) almost overlap, which further indicates the stability of CuDEPP during the electrochemical reaction. An average discharge voltage of 2.8 V (vs. K⁺/K) was measured, which is relatively high compared to other potassium organic cells (Figure 1b). The rate capability of the CuDEPP cathode was tested at different current densities, and discharge capacities of 162, 129, and 119 mAhg⁻¹ were obtained at current densities of 0.1, 0.3, and 0.5 Ag^{-1} within 50 cycles, respectively. Even if the cell was cycled at a current density of 1 Ag⁻¹, a discharge capacity of 104 mAhg⁻¹ could still be achieved. Discharge capacities were mostly restored if the current densities were set back from 1 to 0.1 Ag^{-1} (Figure 1c), which indicates a superior cell durability at high rates. The coulombic efficiency at various current densities was close to 100% after the initial cycles. Selected discharge curves showed that the potential decreased slightly with an increase of the current densities and cycle numbers, which implies a slight increase of polarization during long-term cycling (Figure 1 d).^[50] To further understand the charge-storage mechanism, electrolytes based on different anions were applied to test the charge-storage capability of the CuDEPP cathode. K/CuDEPP half-cells were assembled by using a 0.8 M KTFSI electrolyte in ethylene carbonate (EC) and PC (1:1, v/v). This cell delivered a promising reversible capacity of 106 mAh g⁻¹ (Figure S6 in the Supporting Information). No significant capacity loss was detected in up to 300 cycles at 0.3 Ag^{-1} . These results imply that CuDEPP could be used as a versatile or even universal active material that can adopt different cations and anions for electrochemical energy storage.

To gain more insight into the working mechanism of the CuDEPP in the K-ion half-cell, we conducted postmortem analysis by using ex situ IR spectroscopy, XRD, and XPS. The absorption bands observed in the IR spectra at 3264, 2096, 1600-1460, and 1347 cm⁻¹ correspond to the $-C \equiv C - H$, $-C \equiv C -$, $-C \equiv$ C-, and -C-N- bonds of the as-prepared porphyrin, respectively.^[44,51] The Cu–N band of CuDEPP appeared at 1070 cm⁻¹, and it remained in the spectra of the charged and discharged states. Absorption bands below 1000 cm⁻¹ were assigned to vibrations of C-H. The main absorption bands between 1000 and 2000 cm⁻¹ remained, but they were broadened in the spectra of the charged and discharged states compared to the spectrum of as-prepared CuDEPP. This indicates a change of the electronic structure if anions and cations interacted with the porphyrin complex. A peak at 826 cm⁻¹ for PF₆⁻ appeared in the spectrum of charged CuDEPP (Figure 2a), which confirms the uptake of $\mathrm{PF_6}^-$ at the cathode during the charging process. However, the vibration band did not fully vanish in the spectrum of the discharged material, which suggests a slightly irreversible process in the initial cycles. We used EDX to further confirm the presence of the PF₆ anion in the charged CuDEPP (Figure S7 in the Supporting Information). The C-H stretching band at 3264 cm⁻¹, characteristic of the



Figure 2. (a, b) IR spectra of CuDEPP at various charged states. (c, d) N1s and Cu2p_{3/2} XPS core-level spectra of CuDEPP at different charged states in the first cycle.

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ethynyl group, vanished after the first charging process, which provides clear evidence of the change of the -C=C-H moieties in CuDEPP. Meanwhile, the peak at 2096 cm⁻¹, assigned to the -C=C- vibration, became broader in the spectra of the charged and discharged states, which implies that polymerization occurs during the initial oxidation processes. To further prove this theory, CuDEPP electrodes were prepared at different charged states, as indicated by the "capacities" of 200, 1500, and 2229 mAh g⁻¹, respectively. The IR absorption intensity of the ethynyl group decreased gradually with the increase of the charging time (Figure 2b), which implies the polymerization of the ethynyl group during the charge process, as reported previously.^[44]

To gain more insight into the chemical changes of CuDEPP during the electrochemical process, XPS spectra of the cycled electrodes were recorded (Figure 2 and Figure S8 in the Supporting Information). A main peak at a binding energy (BE) of 398.6 eV was obtained in the N1s spectrum, which is characteristic of the pyrrolic N atom for the as-prepared CuDEPP.^[52] The spectrum showed a weak satellite peak of N at 401.5 eV. After the charging process, the main N1s peak at 398.6 eV was shifted slightly to a higher binding energy of 398.8 eV. Meanwhile, a new peak at 400.5 eV appeared, which is attributed to the interaction between N and the PF₆ anion in the charged state. This was further supported by the F1s core-level spectra, in which new peaks at 687.4 and 684.2 eV were detected. Major peaks in the $Cu 2p_{3/2}$ and $Cu 2p_{1/2}$ core-level spectra at 934.8 and 954.8 eV, respectively, were also observed. The Cu2p spectrum of the as-prepared sample also showed a strong and broad satellite feature between 940 and 945 eV, which indicates the presence of Cu^{II} in CuDEPP. The Cu^{II} was reduced partially to Cu^I during the first cycle (Figure 2d and Figure S8 in the Supporting Information), and an additional peak at 932.6 eV was observed. This phenomenon is usually observed if an anionic ligand is introduced into a metal-organic compound to result in the reduction of the complex ions.[53] In CuDEPP, the reduction of Cu^{II} could also be attributed to the

polymerization of the ethynyl moieties as the C=C bonds are orientated initially with the Cu atoms through a π interaction.^[44] The P2p core-level spectrum shows peaks at 133.4 (P2p_{3/2}) and 137.1 eV (P2p_{1/2}) in charged CuDEPP, which further confirms the interaction between the porphyrin and the PF₆ anion in the charging process (Figure S8 in the Supporting Information). In the discharged state, the intensity of the P2p core-level peak decreased, which suggests the withdrawal of the PF_6 anion upon discharge. In the discharged state (1.7 V), Cu^{II} was partially reduced to Cu^I after the uptake of K (Figure 2 d). Theoretical studies showed that the Cu^{II} ions in the porphyrin were relatively stable upon the withdrawal or uptake of one or two electrons; the result here suggests strongly that Cu^{II} at least partially participates in the electron transfer. In a similar system, it has been confirmed that Ni^{II} in a coordination polymer can be reduced to Ni^I even though Ni^{II} was stable in the compound. Thus, an additional one-electron transfer is enabled during the electrochemical reaction.^[54] Notably, the applied voltage range is greatly important for the contribution of Cu because Cu^{II} can be reduced to Cu⁰ at a low working potential.^[44] No evidence implied the disruption of the complex and the release of Cu in a moderate voltage range in this study. From these results, we conclude that both PF_6^- and K⁺ interact with the CuDEPP cathode during the charge-discharge processes to provide a four-electron-transfer chargestorage mechanism. The complexed Cu^{II} ion participates partially in charge storage to enable an additional electron transfer during the electrochemical reaction. Both cations and anions shuttle between the cathode and anode to provide a highly reversible capacity at various current densities.

DFT simulations were performed to obtain more information on the charge-storage mechanism of both cations and anions in the CuDEPP molecule with the aim to probe the redox site and the redox properties during the electrochemical reaction (Figure 3). The energy difference between the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO of the cycled species is very small (1.5 and 1.4 eV for



Figure 3. Charge-storage sites and energy difference of CuDEPP at different charged states obtained by using DFT.

the charged and discharged CuDEPP, respectively), which is lower than that of as-prepared CuDEPP (2.6 eV) and suggests that the redox reaction takes place at different charging states easily to enable fast kinetics during charge and discharge. This is consistent with the fast charge and discharge capability of CuDEPP shown in Figure 1. PF₆ anions interacted with CuDEPP during the charge process, in which anions were situated at both sides of the porphyrin ring to minimize the energy of the whole system. Upon discharging, two K cations were attached to N atoms in the opposite face of the porphyrin complex (Figure 3). As a result of the electron delocalization within highly conjugated system, both PF_6^- and K^+ ions were well supported to stabilize both the charged and discharged CuDEPP. Notably, the planar structure of CuDEPP was distorted upon the first charge to lead to a bent ring caused by the size effect of the PF₆ anions (Figure S9 in the Supporting Information). We used ex situ XRD to evidence the loss of the crystallinity of the CuDEPP cathode after the first charging process, and no diffraction patterns were detected (Figure 4a). This result agrees with the simulation study, in which the planar porphyrin molecule was bent upon charging to lead to a disordered structure. However, the rodlike shape of the CuDEPP particles was retained upon cycling, except for the clear roughness on the surface with the slight bending of the particle (Figure 4b, c). This observation indicates that the fading of the diffraction patterns is mainly caused by the amorphization rather than the pulverization of CuDEPP. Clearly, the amorphization of CuDEPP is favorable for the electrochemical reaction upon cycling as it could provide sufficient space for the insertion of anions and cations.

If we consider the sloping charge–discharge curves and the amorphization of the CuDEPP electrode during the initial cycles, we expect that the charge-storage mechanism could partially at least show a capacitive contribution. In general, this can be analyzed quantitatively by using a method proposed by Dunn and co-workers^[55] from the relation $i=av^b$, in which *i* is the peak current collected from a certain voltage in the CV curve and *v* is the sweep speed. The *a* and *b* values are usually used to determine the contribution of the ion diffusion process and the pseudocapacitive process, respectively. However, based on the above method, the *b* values cannot be determined precisely because the cathodic and anodic peaks of



Figure 4. (a) XRD patterns of CuDEPP at different charged states in the first cycle. (b, c) SEM image of the as-prepared CuDEPP electrode and after the first cycle.

CuDEPP were not identified as the scanning rate increased (Figure 5a) even through a redox peak at low san rate of 0.1 mV s^{-1} can be observed clearly. From the shape of CV curve, we propose that charge storage is diffusion controlled at a low current density; however, as the scan current is increased, the charge storage contribution comes mainly from the pseuodocapacitive capacity. Electrochemical impedance



Figure 5. (a) CV profiles at different scan rates $(0.1-2 \text{ mV s}^{-1})$. Inset: an enlarged CV profile at a sweep rate of 0.3 mV s⁻¹. (b) EIS spectra and the equivalent circuit model of the cell in the original, 5th, 50th, and 200th cycles.

spectroscopy (EIS) was further applied to study the resistance properties of the cell during the cycling. R_{sr} , R_{ctv} CPE, and Wo of the proposed equivalent circuit represent the contacts and electrolyte resistance, charge-transfer resistance, interfacial capacitance of the electrode–electrolyte, and ion diffusion within the electrode, respectively.^[56] EIS was performed for the 1st, 5th, 50th, and 200th cycles at 0.2 Ag⁻¹ within a frequency range from 100 kHz to 0.01 Hz. The high-frequency semicircle in the Nyquist plots denotes R_{ct} associated with charge-transfer reactions at CuDEPP, which decreased in the initial cycles and increased in the subsequent cycles (Figure 5 b). Before cycling, the



fresh cell showed a larger $R_{\rm ct}$ value (4268 Ω) than after cycling for the 5th (1458 Ω), 50th (789 Ω), and 200th (1814 Ω) cycles. The reduced charge-transfer resistance in the initial cycles can be accounted for by the activation of CuDEPP, which was because electropolymerization occurred through ethynyl groups to lead to an extended π -conjugated framework and high electronic conductivity. However, after 50 cycles, the charge-transfer resistance was generally increased, which could be because of the increase of the surface layer at the CuDEPP. Clearly, the surface layer increased after many cycles (Figure S10 in the Supporting Information).

The electrochemical performance of CuDEPP in a full-cell configuration was also studied, in which graphene was used as a model anode and coupled with the CuDEPP cathode. The graphene material had a stacked and aggregated sheetlike morphology (Figure S11 a in the Supporting Information) and showed typical XRD diffraction patterns (Figure S11b in the Supporting Information). It delivered a discharge capacity of 225 mAh g^{-1} at a current density of 0.2 A g^{-1} (Figure 6a) and demonstrated good cycling stability with a discharge capacity of 207 mAh g⁻¹ after 300 cycles (Figure S11 c in the Supporting Information). A coulombic efficiency of approximately 100% was achieved over 300 cycles except for the initial cycles, which indicated highly reversible potassiation/depotassiation. The excellent K-ion storage in the graphene electrode renders it a good candidate as anode material to explore the performance of CuDEPP. A first discharge capacity of 1600 mAh g⁻¹ was obtained with a distinct plateau at approximately 0.75 V, which was different from that obtained in the second and third cycles (Figure S11 d in the Supporting Information). The reason for the capacity decrease can be attributed mainly to the formation of a solid–electrolyte interphase (SEI) layer and/or partially irreversible K⁺ insertion in the graphene material.^[22] The charge–discharge curves of the cell overlap with negligible polarization in the 100th, 200th, and 300th cycles at a current density of 0.2 Ag^{-1} , which demonstrates its excellent reversible capability (Figure 6b).

The electrochemical performance of a graphene/KPF₆/ CuDEPP full cell in terms of the discharge capacity, coulombic efficiency, and discharge potential was studied (Figure 6 c, d). The cells were tested at a current density of 0.1 Ag⁻¹ between 0.01 and 3.8 V. Discharge capacities were comparatively higher in the initial three cycles than those in other cycles. High capacity retention and coulombic efficiency were also obtained in subsequent cycles, which indicates a highly reversible process. After 700 cycles, a reversible discharge capacity of 50 mAhg⁻¹ was still obtained with a capacity retention of 84%, which corresponds to capacity decay of 0.022% per cycle. The overlapped charge-discharge curves measured for the 100th, 300th, 500th, and 700th cycles reflected the stable capability of the full cell with an average discharge voltage of 2.1 V. A specific energy density of 105 Wh kg^{-1} (based on CuDEPP) at a power density of 210 W kg⁻¹ was obtained. If a higher cutoff potential of 4.0 V was applied (Figure S12 in the Supporting Information), a reversible discharge capacity of 87 mAh q^{-1} was achieved at a current density of 0.1 A q^{-1} after 170 cycles. However, the coulombic efficiency decreased gradually if the cell was cycled up to 120 times, which indicates that side reactions may occur at high cutoff potentials. A good cycling stability was also noted if a cutoff potential of 4.0 V



Figure 6. (a) Cycling performance of the graphene anode over 300 cycles. (b) Selected charge and discharge curves of the K/KPF₆/graphene half-cell at 0.2 A g⁻¹ in a voltage range of 0.01–3.0 V, (c) cycling performance over 700 cycles, and (d) selected charge and discharge curves of the graphene/KPF₆/CuDEPP full cell at 0.1 A g⁻¹ in a voltage range of 0.01–3.8 V.

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was used at 0.2 Ag^{-1} . The full cell was cycled reversibly 400 times, although the coulombic efficiency was lower than that obtained after cycling at 3.8 V (Figure S13a in the Supporting Information). Selected charge–discharge curves at the 100th, 200th, 300th, and 400th cycles exhibited similar curves with an average potential of approximately 2.2 V (Figure S13b in the Supporting Information).

An alloying bismuth anode was tested to further assess the charge-storage capability of the CuDEPP cathode. The Bi anode showed a comparatively higher discharge capacity of 500 mAh g^{-1} at 0.1 A g^{-1} by using 0.8 м of KPF₆ in dimethoxyethane (DME) as an electrolyte to benefit from its high electronic conductivity and the alloying reaction between Bi and K⁺. Nevertheless, a discharge capacity of only 163 mAhg⁻¹ remained after 170 cycles, although the coulombic efficiency approached 100% (Figure S14 in the Supporting Information). As a further step, we constructed a full KIB with a Bi anode, 0.8 M of KPF₆ in DME as the electrolyte, and a CuDEPP cathode (Bi/ KPF₆/CuDEPP). The full cell exhibited a relatively poor electrochemical performance compared to the graphene/KPF₆/ CuDEPP cell in terms of cycling stability (Figure S15 in the Supporting Information). Capacity retentions of 81 and 45% were obtained after initial 30 and 120 cycles, respectively. The capacity loss could be ascribed to potassiation/depotassiation at the Bi anode, which proceeds through an alloying/dealloying reaction.^[26] A suitable anode is crucial to improve the electrochemical performance of the full cell. Therefore, further work will be performed to optimize different anode materials and electrolytes to better support the CuDEPP cathode.

A comparison of the electrochemical performance of the CuDEPP cathode with the reported KIB cathodes is shown in Figure 7. Compared to the limited potassium-ion storage sites in inorganic layered compound, multielectron transfer in the porphyrin ring enables a higher reversible capacity. The presence of both anions and cations as charge carriers in CuDEPP offers an average potential of 2.8 V, which take it to the high-energy-density region of the proposed potassium organic cathodes. More details of reported KIB cathodes are summarized in Table S1 in the Supporting Information. Compared to other or-



Figure 7. Comparison of the electrochemical performance of potassium-based batteries with different cathode materials in terms of the specific capacity, average operating voltage, and energy density.

ganic cathodes, CuDEPP can endure a higher current density during the electrochemical reaction because of the electropolymerization through the ethynyl groups of the porphyrin molecule, which leads to a better power density and energy density.

Conclusions

A functionalized porphyrin complex of [5,15-bis(ethynyl)-10,20diphenylporphinato]copper(II) (CuDEPP) has been investigated as a new cathode material for potassium organic rechargeable batteries. A charge storage mechanism of the porphyrin that involves multielectron transfer and a self-stabilization process has been proposed. The facile multielectron uptake and release at the delocalized porphyrin macrocycle enables both high energy and power density. In addition, the ordered CuDEPP changed irreversibly to an amorphous phase after polymerization in the first cycle, which is beneficial for the intercalation/deintercalation process at the near surface of CuDEPP. The CuDEPP cathode delivered a good reversible capacity of 181 mAhg⁻¹ with an average voltage of 2.8 V (vs. K⁺/ K) and a capacity retention of 87% over 300 cycles. A high energy density of 408 Wh kg⁻¹ at a power density of 859 W kg⁻¹ was achieved in a K-based half-cell. Moreover, a potassium-metal-free energy-storage device was also assembled flexibly with a CuDEPP cathode paired with a graphene anode, which realized a remarkably high cycling stability with a capacity retention of 84% after 700 cycles. This finding opens opportunities to design new porphyrin-based materials for highperformance potassium-ion batteries.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: copper · energy storage · macrocycles · porphyrinoids · potassium

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