

New Organic Electrode Materials for Ultrafast Electrochemical Energy Storage

Zhirong Zhao-Karger, Ping Gao, Thomas Ebert, Svetlana Klyatskaya, Zhi Chen, Mario Ruben,* and Maximilian Fichtner*

Organic materials are both environmentally and economically attractive as potential electrode candidates. This Research News reports on a new class of stable and electrically conductive organic electrodes based on metal porphyrins with functional groups that are capable of electrochemical polymerization, rendering the materials promising for electrochemical applications. Their structural flexibility and the unique highly conjugated macrocyclic structure allows the produced organic electrodes to act as both cathode and anode materials giving access to fast charging as well as high cycling stability. The extreme thermal and chemical stability of the porphyrin-based organic electrodes and their chemical versatility suggest an important role for these molecular systems in the further development of novel electrochemical energy storage applications.

well as on the resulting charging times, which have to be considerably cut in comparison to the state of the art. Due to the challenge on storage capabilities, sustainability, safety, and high cost, conventional rechargeable Li-batteries may not be able to satisfy the ever-increasing demand for energy storage in certain application areas, e.g., electro-mobility and electric power grid. Organic batteries are regarded as promising candidates for the future generation electrochemical energy storage due to their low-cost, recyclability, resource sustainability, environmental friendliness, structural diversity, and flexibility. Herein, we report on the novel porphyrin-based

1. Introduction

Electrochemical energy storage (EES) technology is one of the most promising means to store the electricity in large- and small-scale applications because of its flexibility, high energy conversion efficiency, and simple maintenance. Rechargeable batteries and supercapacitors with high efficiency, low cost, long cycle life, and high safety are desired. Rechargeable lithium-ion batteries using inorganic cathode materials are currently the basis for most portable electronic devices. In the near future, many applications like the usage in electronic vehicles will crucially depend on an improved performance but also on easy availability and moderate costs of the active materials as

electrode materials extending their use toward electrochemical applications, which might be replacement of both anode and the conventional inorganic cathode in rechargeable Li-ion batteries. The reported results advent potential access to thin-film batteries, rechargeable batteries, redox flow batteries, and even all-organic, flexible batteries designs.

2. Porphyrin-Based Complexes in Electrochemical Energy-Storage Systems

Porphyrins and related structures are wide-spread in nature and show interesting properties that give them key roles in different biological processes. For instance, they are the central structural motifs in, e.g., hemoglobin and chlorophyll and can be considered pivotally for basic processes of life. Porphyrins are extensively conjugated planar macrocyclic systems and exhibit excellent light-harvesting and efficient electron transferring abilities. Consequently, porphyrins have been intensively investigated in the field of photovoltaic applications.^[1,2] In addition, due to their small highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps that enable fast electron uptake and release,^[3] porphyrins exhibit high redox activities and can be potentially used for EES devices. Recently, porphyrin-based active materials have drawn great interest as new class of organic electrodes for supercapacitors,^[2,3] rechargeable batteries,^[4–6] and redox-flow batteries.^[7] Low conductivity and high solubility in the organic electrolyte are generally two main drawbacks of organic electrode materials.^[8] In contrast, porphyrin-derived synthesis strategies have substantial advantages in modifying the structure and composition of the organic electrode materials synergistically with insolubility and high electric conductivity. From this perspective, we highlight some emerging applications of

Dr. Z. Zhao-Karger, Dr. P. Gao, Dr. T. Ebert, Prof. M. Fichtner
Helmholtz Institute Ulm
89081 Ulm, Germany
E-mail: m.fichtner@kit.edu

Dr. S. Klyatskaya, Dr. Z. Chen, Prof. M. Ruben
Prof. M. Fichtner, Institute of Nanotechnology
Karlsruhe Institute of Technology
Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
E-mail: mario.ruben@kit.edu

Prof. M. Ruben
Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS
Université de Strasbourg
23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201806599>.

© 2019 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/adma.201806599

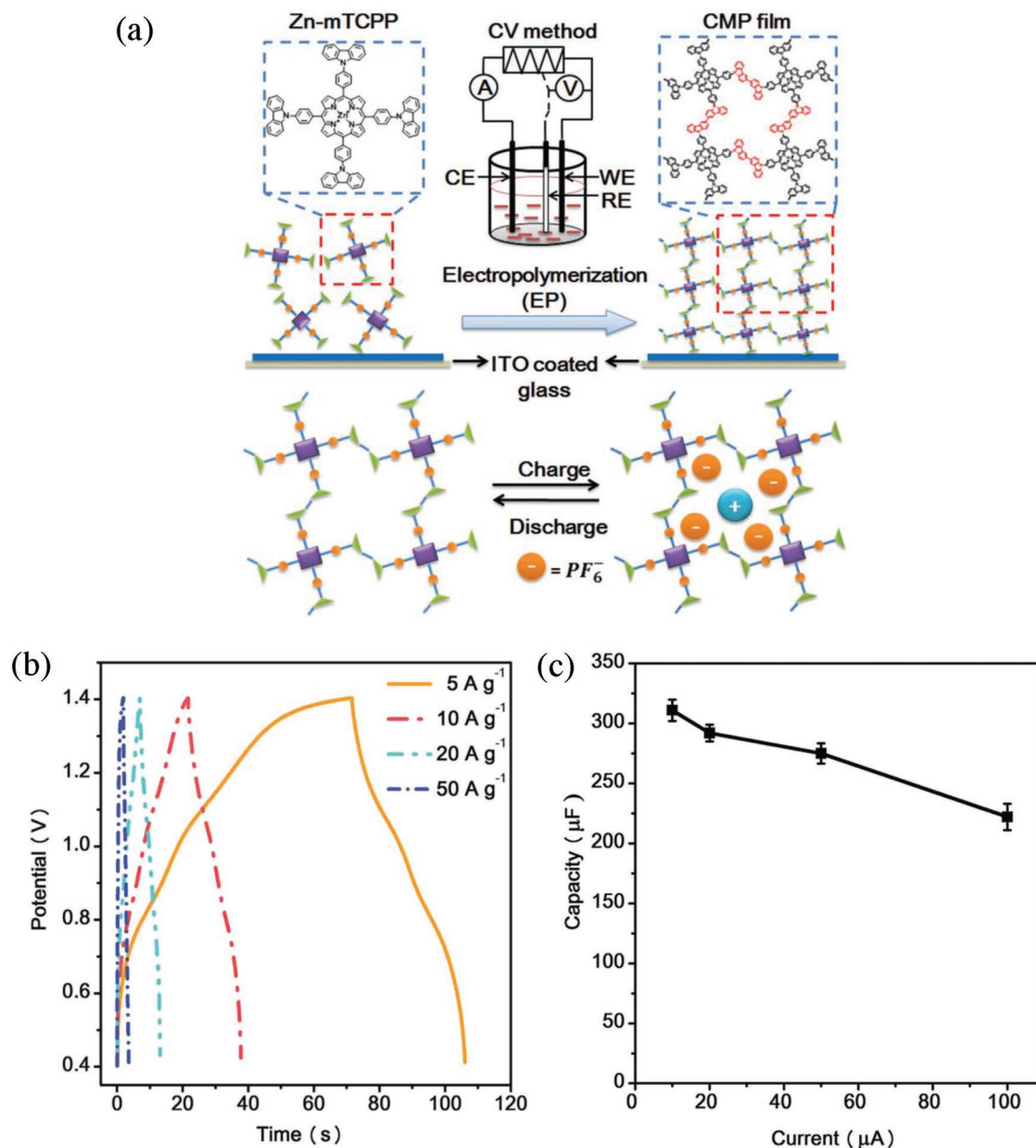


Figure 1. a) Illustration of the electropolymerization technique for the preparation of zinc-porphyrin based CMP film. b) Galvanostatic charge/discharge curves at different current densities. c) Capacitance retention of the CMP film electrodes at different current densities. Reproduced with permission.^[4] Copyright 2015, John Wiley and Sons.

porphyrin-related structures as electrode materials for electrochemical devices with the aim to shed light on the further exploration of this new application area of porphyrins in addition to their conventional uses.

2.1. Porphyrin-Based Polymers in Capacitive Energy Storage

Zinc porphyrin-based conjugated microporous polymers (CMPs) have been reported as functional and stable porous film materials for the usage in supercapacitors.^[4] Figure 1a shows the synthetic process, where the precursor Zn (II)

5,10,15,20-tetrakis[(carbazol-9-yl)phenyl]porphyrin (Zn-mTCPP) undergoes electrochemical polymerization through the *N*-substituted carbazole groups as an active linker. The yielded CMP films possess a cross-linked 3D network structure and high surface area, which could greatly facilitate ion transportation. In addition, the redox active Zn porphyrin cores and the electron conductive carbazole linkages render the Zn-mTCPP based polymer a promising electrode active material. Consequently, high-performance capacitive energy storage has been demonstrated with the Zn-mTCPP based films. As shown in Figure 1b,c, the film electrode can be operated at a current density above 5 A g⁻¹ offering high power supply and a maximum capacitance of

142 F g⁻¹, which is among the highest values of reported conducting polymer electrodes.

Another porphyrin-based electrode materials used for supercapacitor was constructed by incorporating an organic radical redox units of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the covalent organic framework (COF) synthesized from nickel 5,10,15,20-tetrakis(4'-tetraphenylamino) porphyrin (NiP).^[5] In such type of crystalline porous COFs, the organic functional groups are covalently immobilized offering an outstanding structural stability, and the ordered pore structure allows for high-rate ion transport and easy access to the redox sites within the materials. These unique structural features make the porphyrin-based COFs an attractive material for energy storage.

2.2. Porphyrin-Based COF Materials for Lithium Storage

The first 2D COF used as an anode for lithium-ion batteries has been reported,^[9] in which a high conductive polyporphyrin (TThPP) linked by 4-thiophenophenyl groups was synthesized through a chemical oxidative polymerization on the surface of copper foils (Figure 2a). The TThPP film exhibits promising structural properties for use as electrode material with insolubility and high electric conductivity. It possesses a large surface for adsorption of Li atoms. The ordered channels enable fast Li-ion transport and the alignment of polyporphyrin nanosheets via the covalent π - π electron interaction enable facile electron transfer within the structure, which results in a high capacity and excellent rate performance. As shown in Figure 2b,c, the TThPP film electrode can be operated at the current density up to 4 A g⁻¹, and showed a stable discharge capacity of 381 mAh g⁻¹ and Coulombic efficiency of 99% over 200 cycles at a current density of 1 A g⁻¹.

2.3. Functionalized Porphyrins for High-Performance Batteries

The first use of porphyrin in Li-based batteries was demonstrated by Shin et al.,^[6] where dimesityl-substituted norcorrole nickel (II) complex (NiNC) was examined as a cathode material. With a Li metal foil anode, the Li-NiNC batteries exhibited an average battery voltage of 2.5 V and stable reversible capacity of \approx 200 mAh g⁻¹ over 100 cycles at a current density of 1 mA g⁻¹. The redox mechanism was proposed to be a two-electron oxidation and two-electron reduction of the antiaromatic NiNC forming their stable 14 π and 18 π aromatic dicationic and dianionic species, respectively. However, while a proof-of-concept of battery chemistry based on redox reactions between aromatic and antiaromatic chemical structures has been shown, antiaromatic compounds are, in general, unstable and need high synthetic efforts,^[10] which may limit their practical applications.

In this respect, the stable porphyrin complex [5,15-bis(ethynyl)-10,20-diphenylporphyrinato]copper(II) (CuDEPP) with a π -stacked structure has been shown to act as very versatile and promising active material in different battery systems (Figure 3).^[11] The electrochemical mechanism of the CuDEPP electrode material is supposed to be based on the redox reactions at the porphyrin cores, where the 18 π -electron aromatic CuDEPP system can be oxidized and reduced to the 16 π - and 20 π -electron

macrocyclic systems, respectively (Figure 3b). Such type of redox reactions have been proved in the analogous porphyrin derivatives such as Cu(II) complex of 5,10,15,20-tetraphenylporphyrin (CuTPP).^[12] As the CuDEPP have interesting bipolar properties with the capabilities of donating and accepting electrons, two different types of batteries have been investigated, where the cell 1 using CuDEPP as a cathode and Li metal as an anode, whereas cell 2 CuDEPP works as an anode coupled with an graphite cathode and an ionic liquid electrolyte (Figure 1c).

Despite the interesting redox chemistries, most of porphyrins are soluble in organic solvents, which limit their usage as electrode materials. In fact, 5,10,15,20-tetraphenylporphyrin (H2TPP) has been recently demonstrated to be used as the active material for redox-flow batteries.^[7] In contrast, the CuDEPP with two ethynyl substituents has a low solubility. Moreover, the ethynyl groups can undergo electrochemically polymerization and act as functional linkages connecting the porphyrin units into an extended π -conjugated framework with high electric conductivity. The oxidative polymerization of CuDEPP has been proved by analyzing the electrode materials at different charge/discharge states, where the characteristic ethynyl stretching vibrational modes of the C \equiv C and \equiv C-H bonds vanished and at the same time the insertion of PF₆⁻ was verified after the charging process (Figure 3e). Furthermore, the density functional theory (DFT) calculations also confirm the trend of the polymerization of CuDEPP, where increasing HOMO and decreasing LUMO levels were calculated with increasingly forming chain length (Figure 3f). This smaller HOMO-LUMO gap of CuDEPP may lead to facile electron-transfer and an increased conductivity. The increase of the conductivity of the electrodes was evidenced by a reduced resistivity found in electrochemical impedance spectroscopy. These beneficial features for fast redox reactivity have been reflected in the remarkably high rate capability of the CuDEPP-based cathodes. After 20 formation cycles at a relatively low current of 200 mA g⁻¹, which have been described as "self-conditioning" process, the cell 1 can be operated at a current rate as high as 10 A g⁻¹ (53C), delivering a discharge capacities of 115 mAh g⁻¹ within 42 s (Figure 3g,h). When the charge rates were reduced to 1 A g⁻¹, the initial values of the discharge capacities were restored, which proves the excellent rate capability and mechanistic robustness of this material. The cycling stability of the cell 1 has been investigated at a current density of 4 A g⁻¹ (Figure 3f), where the CuDEPP cathode can be operated for more than 8000 cycles with 60% capacity retention. The selected voltage profiles indicate that an average discharge voltage of about 3 V can be maintained upon long-term cycling (Figure 3i). Furthermore, the Coulombic efficiency increases during the first cycles and remains close to 100% during the subsequent cycles. Thus, the cell 1 can reach gravimetric energy densities of 345 Wh kg⁻¹, while having power densities as high as 29 kW kg⁻¹. Taking the excellent cycling stability into account, these results are superior to most other organic electrode materials, suggesting that CuDEPP is competitive with conventional inorganic materials and could be used as a cathode in lithium-ion cells.

Moreover, it is also possible to use CuDEPP as active material in lithium-free cells. To demonstrate this, a CuDEPP-based electrode has been used in a dual-ion-battery with graphite

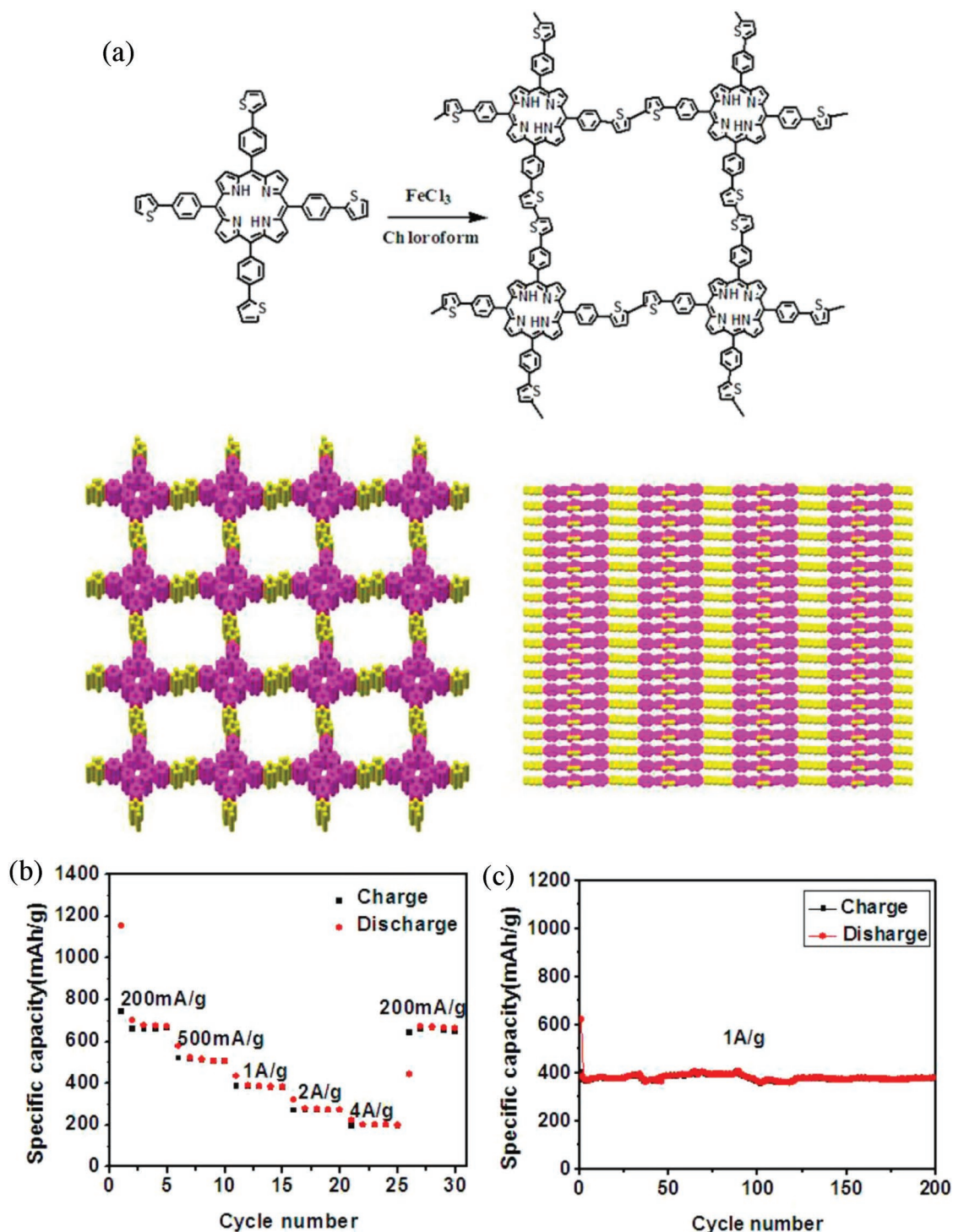


Figure 2. a) Scheme of the synthesis and the DFT structure model of TThPP (porphyrin: pink, thiophene: yellow, H atoms are omitted for clarity). b) Rate capability, c) cycling performance of the TThPP film anode. Reproduced with permission.^[9] Copyright 2016, American Chemical Society.

as working electrode and 1-butyl-1-methylpiperidinium bis-(trifluoromethylsulfonyl)imide (PP14TFSI) as electrolyte as illustrated as cell 2 in Figure 1c. CV investigations of this system show peaks that agree well with the insertion and deinsertion processes that have been described in the literature.^[13] The cell was charged and discharged at 1 A g⁻¹ showing a discharge

capacity of 94 mAh g⁻¹ in the first cycle and around 80 mAh g⁻¹ in the subsequent cycles. This is consistent with the calculated theoretical specific capacity 94 mAh g⁻¹ as two electrons per CuDEPP molecule are transferred in this particular setup. At a high current rate of 5 A g⁻¹, a discharge capacity of around 44 mAh g⁻¹ and an average cell potential of around 2.0 V were

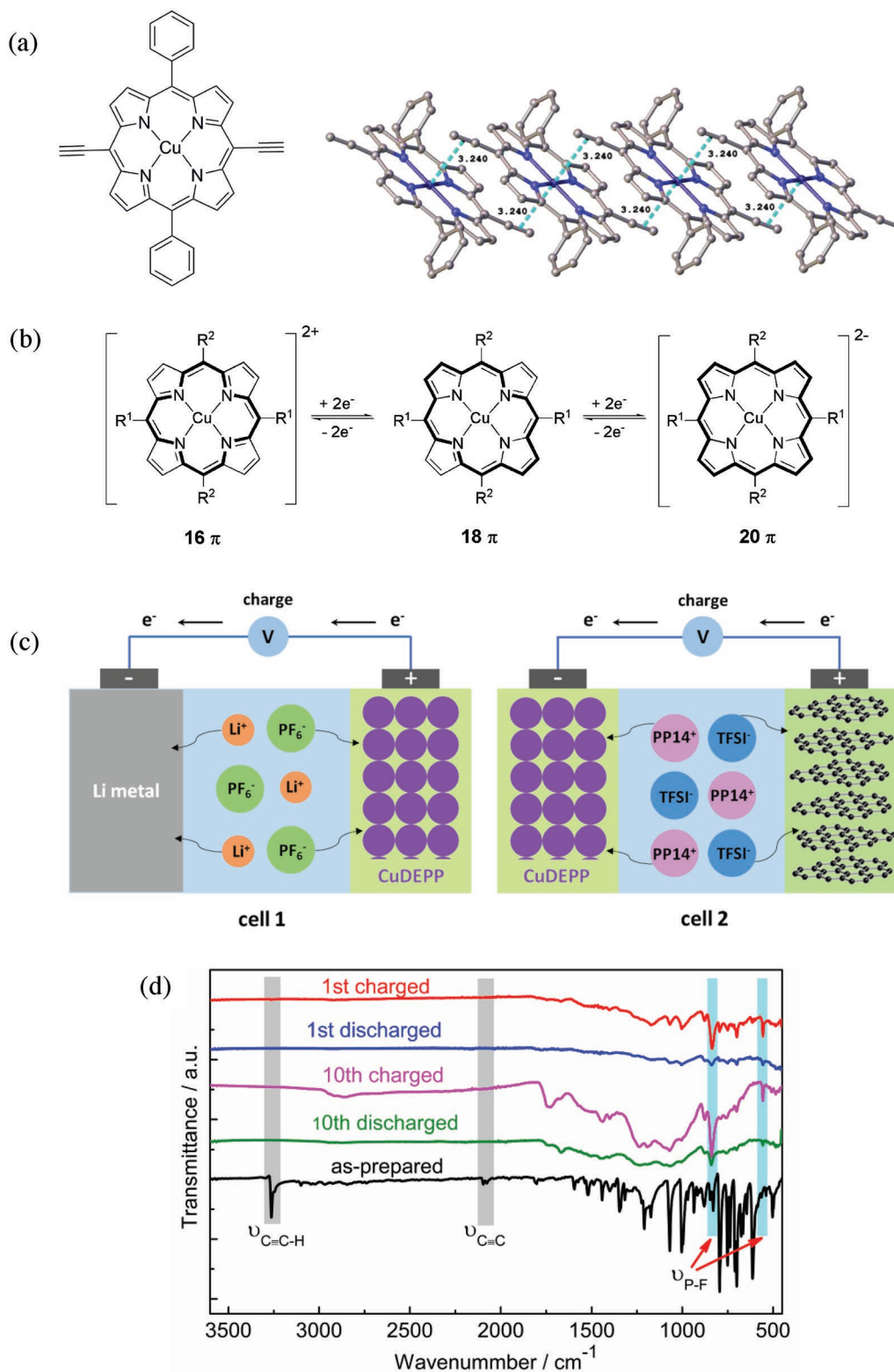


Figure 3. a) Chemical and crystal structure of CuDEPP. H atoms are omitted. b) Mesomeric structures of the oxidation and reduction of porphyrin. The bold line marks the conjugated π -electron ring systems. c) Cell configurations. d) IR spectra of the CuDEPP electrode at different charge stages. e) Energy level diagram based on DFT-B3LYP calculations. The HOMO/LUMO plots of CuDEPP (from left to right) the -2 charged state, the neutral state, the neutral state of a dimer and their associated energies relative to vacuum level (E_{vac}), along with the HOMO-LUMO gap. f) Rate capability, g) cycling stability of the CuDEPP cathode in cell 1. h) Discharge curves of the CuDEPP cathode in different cycles at various current rates. i) Charge/discharge voltage profiles of the CuDEPP cathode in the selected cycles at a rate of 4 A g^{-1} . Reproduced with permission.^[11] Copyright 2016, John Wiley and Sons.

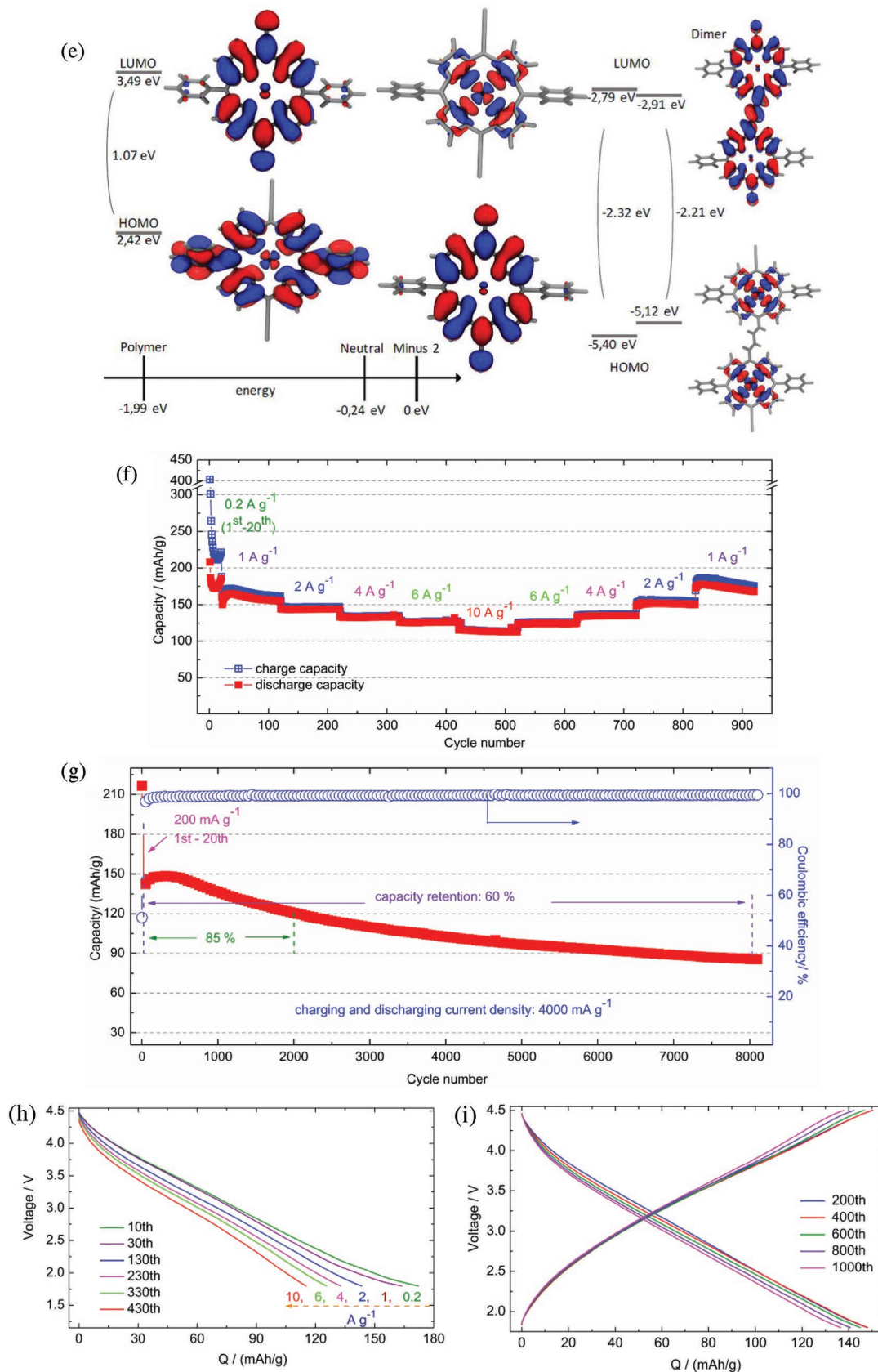


Figure 3. Continued.

retained after more than 200 cycles. Additionally, a high current rate up to 10 A g⁻¹ (106C) has been applied to the cell 2, where a discharge capacity of 32 mAh g⁻¹ was delivered within just 12 s, which corresponds to a power density of 14 kW kg⁻¹.

These results demonstrate that CuDEPP can be used as a high-performance and versatile electrode material for energy storage and hold an attractive potential for further investigations and applications. Compared with the above-mentioned other systems, there is no need for a separate synthesis of the polymer as this takes place in a self-condition step simultaneously to the charging process in the first cycles.

3. Summary and Perspectives

Porphyrin and its derivatives, highly conjugated π -electron macrocycles with unique redox properties, have been demonstrated as powerful molecular building blocks for the design of novel organic electrode materials. The promising chemical/electrochemical properties desired in organic electrode materials, including low insolubility, high electric conductivity, fast ion, and charge transport and efficient storage abilities, may be realized in porphyrin-derived materials by proper molecular engineering. Porphyrin-based COFs represent a feasible solution for electrode materials simultaneously achieving fast ion transport and high electronic conductivity owing to their open framework structures and the unique π - π interactions within the porphyrin units. The porphyrin precursor CuDEPP has been shown to act as highly promising molecular electrode material in various battery systems. A stable rate capacity and high energy density at a high specific power has been demonstrated. In contrast to the slow discharge/charge processes in conventional Li-batteries, the presented organic electrodes are capable of self-conditioning through electrochemical polymerization, exhibiting a rapid redox conversion involving up to four electrons transfers. Half-cells using CuDEPP in cathodes possess power densities in the range of supercapacitors, while providing energy capacities as high as ordinary lithium-ion batteries.

A further focus in the continuing studies is on the variation of the chemical structure to promote the general concept of a self-conditioning and self-stabilizing electrode material and extend it to other organic structures. The influence of the modification of the molecular structure on the performance of the active material is currently under investigation. Possible chemical modifications include the central metal atom, the coordinating heteroatoms or the substituents of the porphyrin.

Overall, the multifunctional porphyrins as electrode materials and their outstanding properties open up new pathways for the design of fast supercapacitors, thin-film batteries, aqueous rechargeable batteries, redox flow batteries, and even all-organic flexible batteries. Moreover, porphyrin based electrode may also be employed for beyond Li-ion and multivalent metal batteries. Very recently, porphyrin-based organic-framework hollow spheres have been used as part of cathodes to chemically adsorb but also physically entrap sulfur in lithium-sulfur batteries or in composites with carbon nanotubes as catalyst for zinc-air batteries.^[14,15]

Considering their interesting properties and promising applications, the design and synthesis of new porphyrin-functionalized electrode is highly demanded. In future studies, theoretical calculation and computational modeling might significantly facilitate the studies on new porphyrin-based materials for electrochemical applications.

Acknowledgements

Funding by the German Research Foundation (DFG) priority programmes 1928, TR88 "3Met" and the KNMF facility (KIT, Germany). This study was supported by China Scholarship Council (CSC) and MagS project (3XP0032E) of German Ministry of Research and Education (BMBF). This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe).

Note: The full citation for ref. [4] was added on June 24, 2019, after initial publication online.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrochemical applications, electrochemical polymerization, organic electrodes, porphyrin-based electrode materials

Received: October 11, 2018

Revised: December 17, 2018

Published online: February 20, 2019

- [1] L. L. Li, E. W. G. Diau, *Chem. Soc. Rev.* **2013**, *42*, 291.
- [2] A. Mahmood, X. Wang, *J. Mater. Chem. A* **2018**, *6*, 16769.
- [3] M. S. Liao, S. Scheiner, *J. Chem. Phys.* **2002**, *117*, 205.
- [4] H. Zhang, Y. Zhang, C. Gu, Y. Ma, *Adv. Energy Mater.* **2015**, *5*, 1402175.
- [5] F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu, D. Jiang, *Angew. Chem., Int. Ed.* **2015**, *54*, 6814.
- [6] J. Y. Shin, T. Yamada, H. Yoshikawa, K. Awaga, H. Shinokubo, *Angew. Chem., Int. Ed.* **2014**, *53*, 3096.
- [7] T. Ma, Z. Pan, L. Miao, C. Chen, M. Han, Z. Shang, J. Chen, *Angew. Chem., Int. Ed.* **2018**, *57*, 3158.
- [8] S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka, U. S. Schubert, *Chem. Rev.* **2016**, *116*, 9438.
- [9] H. Yang, S. Zhang, L. Han, Z. Zhang, Z. Xue, J. Gao, Y. Li, C. Huang, Y. Yi, H. Liu, Y. Li, *ACS Appl. Mater. Interfaces* **2016**, *8*, 5366.
- [10] T. Kakui, S. Sugawara, Y. Hirata, S. Kojima, Y. Yamamoto, *Chem. - Eur. J.* **2011**, *17*, 7768.
- [11] P. Gao, Z. Chen, Z. Zhao-Karger, J. E. Mueller, C. Jung, S. Klyatskaya, T. Diemant, O. Fuhr, T. Jacob, R. J. Behm, M. Ruben, M. Fichtner, *Angew. Chem., Int. Ed.* **2017**, *56*, 10341.
- [12] M. Inamo, H. Kumagai, U. Harada, S. Itoh, S. Iwatsuki, K. Ishihara, H. D. Takagi, *Dalton Trans.* **2004**, 1703.
- [13] T. Placke, S. Rothermel, O. Fromm, P. Meister, S. F. Lux, J. Huesker, H.-W. Meyer, M. Winter, *J. Electrochem. Soc.* **2013**, *160*, A1979.
- [14] B. Q. Li, S. Y. Zhang, L. Kong, H. J. Peng, Q. Zhang, *Adv. Mater.* **2018**, *30*, 1707483.
- [15] B. Q. Li, S. Y. Zhang, B. Wang, Z. J. Xia, C. Tang, Q. Zhang, *Energy Environ. Sci.* **2018**, *11*, 1723.