



Rechargeable Batteries

International Edition: DOI: 10.1002/anie.201702805 German Edition: DOI: 10.1002/ange.201702805

A Porphyrin Complex as a Self-Conditioned Electrode Material for High-Performance Energy Storage

Ping Gao⁺, Zhi Chen⁺, Zhirong Zhao-Karger,* Jonathan E. Mueller, Christoph Jung, Svetlana Klyatskaya, Thomas Diemant, Olaf Fuhr, Timo Jacob, R. Jürgen Behm, Mario Ruben,* and Maximilian Fichtner*

Abstract: The novel functionalized porphyrin [5,15-bis-(ethynyl)-10,20-diphenylporphinato]copper(II) (CuDEPP) was used as electrodes for rechargeable energy-storage systems with an extraordinary combination of storage capacity, rate capability, and cycling stability. The ability of CuDEPP to serve as an electron donor or acceptor supports various energystorage applications. Combined with a lithium negative electrode, the CuDEPP electrode exhibited a long cycle life of several thousand cycles and fast charge-discharge rates up to 53 C and a specific energy density of 345 Wh kg^{-1} at a specific power density of 29 kW kg⁻¹. Coupled with a graphite cathode, the CuDEPP anode delivered a specific power density of $14 \, kW kg^{-1}$. Whereas the capacity is in the range of that of ordinary lithium-ion batteries, the CuDEPP electrode has a power density in the range of that of supercapacitors, thus opening a pathway toward new organic electrodes with excellent rate capability and cyclic stability.

Long-term success in electric mobility and grid-scale energy storage requires electrochemical energy-storage (EES) systems with high energy, high power, long cycle life, reliable safety, and low cost.^[1–3] Conventional lithium-ion batteries

[*]	Dr. P. Gao, ^[+] Dr. Z. Zhao-Karger, Dr. J. E. Mueller, C. Jung, Prof. Dr. T. Jacob, Prof. R. J. Behm, Prof. Dr. M. Fichtner Helmholtz Institute Ulm (HIU) Helmholtzstrasse 11, 89081 Ulm (Germany) E-mail: zhirong.zhao-karger@kit.edu m.fichtner@kit.edu
	Dr. Z. Chen, ^[+] Dr. S. Klyatskaya, Dr. O. Fuhr, Prof. Dr. M. Ruben, Prof. Dr. M. Fichtner
	Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT) P.O. Box 3640, 76021 Karlsruhe (Germany) E-mail: mario.ruben@kit.edu
	Dr. T. Diemant, Prof. R. J. Behm Institute of Surface Chemistry and Catalysis, Ulm University Albert-Einstein-Allee 47, 89081 Ulm (Germany)
	Dr. O. Fuhr Karlsruhe Nano-Micro Facility (KNMF) Karlsruhe Institute of Technology (KIT) (Germany)
	Prof. Dr. T. Jacob Institute of Electrochemistry, Ulm University Ulm (Germany)
	Prof. Dr. M. Ruben Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS) CNRS-Université de Strasbourg (France)
[+]	These authors contributed equally.
D	Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201702805.

(LIBs) based on inorganic materials possess the highest energy density among the current EES systems, but have a low power output because of the slow charge/discharge kinetics.^[4,5] In contrast, electrochemical capacitors (ECs) are known as high-power EES systems; however, they exhibit low energy densities owing to the limited surface charge-storage capabilities.^[6–8] Furthermore, the use of transition-metalbased electrode materials raises critical concerns regarding the depletion of resources as well as expensive and environmentally unfriendly production.^[9]

The affordability and innocuous and biologically friendly nature of organic materials make them both environmentally and economically attractive. Considerable effort has been devoted to the development of organic electrodes for rechargeable batteries, redox-flow batteries, and supercapacitors.^[10–16] However, the present organic electrode materials suffer from low electrical conductivity and dissolution into the electrolyte.^[13,14] Accordingly, the improvement of rate capability and cyclability is the major challenge for research on organic electrodes.

Porphyrins are ubiquitous in nature and perform essential functions of life.^[17] The attractive electronic emission and absorption properties of porphyrin compounds have been investigated for light harvesting and catalytic applications.^[18-20] Shin et al. initally reported the use of a norcorrole nickel(II) complex as an electrode material in batteries, the mechanism for which was proposed on the basis of the transformation from antiaromatic to aromatic states of the porphyrin.^[16] In fact, 16π and 20π porphyrins, produced by oxidizing or reducing the 18π porphyrins, have been successfully isolated,^[21-23] thus suggesting that porphyrins might serve as bipolar organic electrodes by donating or accepting electrons at its mesomeric core. Moreover, porphyrins generally have small HOMO-LUMO gaps that enable the facile uptake and release of electrons, thus leading to fast redox kinetics.^[24] The use of a porphyrin-based polymer as an electrode in supercapacitors has been reported.^[25] Recently, porphyrin-based covalent organic frameworks (COFs) have been investigated for EES. The redox activity of the COFs relied on the functional groups on the porphyrin, and their capacity was limited by the relatively high molecular weights.^[26,27]

Taking the high synthetic cost of antiaromatic porphyrins into consideration, we were interested in exploring stable and readily accessible 18π porphyrins as potential electrode materials for EES. Theoretical calculations show that the first redox reaction in porphyrin complexes with copper occurs at the ligand, whereas Cu^{II} remains in its initial +2

Angew. Chem. Int. Ed. 2017, 56, 10341-10346



oxidation state.[27,28] To avoid the structural changes induced by the redox reaction of the central metal, we envisaged that Cu^{II} porphyrin complexes would be wellsuited for use as electrode materials in batteries. [5,10,15,20-Tetraphenylporphinato]copper(II)

(CuTPP) was initially probed in a lithiumbased cell; the performance, however, was unsatisfactory, probably because of its high solubility in the electrolyte (see Figure S1 in the Supporting Information). In the light of studies on the beneficial effects of terminal alkyne groups on the electronic conductivity and electrochemistry of porphyrins,^[29–32] we synthesized a new porphyrin complex, [5,15-bis-(ethynyl)-10,20-

diphenylporphinato]copper(II) (CuDEPP), and investigated its redox properties for EES.

CuDEPP was readily synthesized and characterized by spectroscopic and microscopic methods Figures S2–S4). (see Scanning electron microscopy (SEM) revealed that



cell 1

Figure 1. a) Chemical structure of CuDEPP. b) Crystal structure (H atoms are omitted). c) Mesomeric transformations (R^1 = ethynyl, R^2 = phenyl; the bold line shows the π -conjugation circuit). d) Cell configurations. PP14 TFSI = 1-butyl-1-methylpiperidinium bis (trifluoromethylsulfonyl)imide.

the CuDEPP crystals were nanorods with a length of about 4 µm and diameters between 200 and 400 nm (see Figure S5). Owing to its low solubility in organic solvents, CuDEPP could not be recrystallized for X-ray crystallography. The crystal structure of CuDEPP was determined by means of powder Xray diffraction (XRD; see Figure S6). Single crystals of the precursor complex [5,15-bis(trimethylsilylethynyl)-10,20diphenylporphinato]copper(II) (CuDEPP-TMS) were isolated, and their structure determined by crystallographic methods (see Figures S7-S9). Both CuDEPP-TMS and CuDEPP crystallized in a triclinic system with the space group $P\overline{1}$ (see Figures S10 and S11). The packing structure of CuDEPP showed that the porphyrin rings stack parallel to one another with offset centers, and that Cu sits between the C-C triple bonds of neighboring porphyrin molecules (Figure 1b). The interplanar separation in CuDEPP is about 3.2 Å. Thermogravimetry-differential scanning calorimetry analysis (TGA-DSC) and infrared (IR) spectra at different temperatures indicated that CuDEPP is thermally stable up

a two-electron reduction to form a dicationic species (CuDEPP²⁺, 16 π) and a dianionic species (CuDEPP²⁻, 20 π),

respectively (Figure 1 c). To explore the intriguing reactivity of CuDEPP as an electron donor-acceptor, we designed two different cells according to the corresponding redox mechanisms (Figure 1 d): In cell 1, the CuDEPP electrode is coupled with a Li negative electrode in a LiPF₆ electrolyte; in cell 2, CuDEPP is used as an anode paired with a graphite cathode in an ionic-liquid electrolyte.

to 220°C in air (see Figures S12 and S13), which may be

impedes cyclic voltammetric (CV) analysis. On the basis of

the reported redox chemistry of the analogous compound

CuTPP,^[33] we propose that the electrooxidation/-reduction of

CuDEPP proceeds by a reversible two-electron oxidation and

attributed to its aromatic nature and π -stacked structure. The low solubility of CuDEPP in common solvents

To determine the working-potential window for cell 1, we first recorded the CV in a voltage range from 4.5 to 0.05 V by using CuDEPP as the working electrode and Li foil as the



Figure 2. a) CV in the range of 4.5–0.05 V. b) CV in the range of 4.5–1.8 V at a scan rate of 0.1 mVs⁻¹. c) Charge and discharge profiles at 200 mAg⁻¹. d) dQ/dV plots of the discharge curves in (c).

counterelectrode and reference electrode. During the first anodic sweep, a distinct irreversible oxidative peak appeared at 4.2 V (Figure 2 a), thus suggesting a reaction between the electrode and electrolyte. We hypothesize that the CuDEPP might be changed at the ethynyl substituents in this oxidation process, as discussed in detail later. (To differentiate it from the initial CuDEPP, the porphyrin core after the anodic reaction is denoted [CuDEPP]). The oxidation of [CuDEPP] to [CuDEPP]²⁺ might also occur during the initial anodic scan. The subsequent cathodic peaks at 3.62 and 2.34 V might be correlated to the reduction reactions [CuDEPP]²⁺ + $2 e^- \leftrightarrow$ [CuDEPP] and [CuDEPP] + $2 e^- \leftrightarrow$ [CuDEPP]²⁻,

respectively. The lowest irreversible reductive signals at 1.27 and 0.78 V are probably associated with the reduction of Cu^{II} to Cu^0 (Figure 2 a), as verified by ex situ X-ray photoelectron spectroscopy (XPS; see Figure S14). In the reverse scan, the absence of anodic signals implies irreversible changes of the electrode as a result of a chemical reaction of the porphyrin. In contrast, the CV in the voltage range of 4.5–1.8 V exhibited reversible redox pairs at 2.22/2.95 V and 3.55/3.68 V after the first anodic scan (Figure 2b), which are assigned to the reversible reactions between [CuDEPP]²⁺ and [CuDEPP]²⁻ described above.

On the basis of the CV results, the voltage range of 4.5-1.8 V was utilized in the galvanostatic tests for cell 1. Figure 2c shows a flat voltage plateau at about 4.1 V for the initial charging, which is consistent with the above-described irreversible feature in the CV. After the first charging process, a highly reversible discharge/charge event is indicated. According to the mass of CuDEPP (50 wt% of the total electrode), the discharge capacity of 182 mAh g⁻¹ in the 3rd cycle is close to the theoretical value of $187 \,\mathrm{mAh\,g^{-1}}$ correlated to the four-electron reaction $[CuDEPP]^{2+} \leftrightarrow$ [CuDEPP]²⁻. The capacity contribution of carbon black of 5 mAh g^{-1} is neglected herein (see Figure S15). No welldefined voltage plateau is present in the charge/discharge profiles, thus indicating rapid multiple redox reactions without clear phase transitions. A similar sloping curve has often been observed in organic electrodes with pseudocapacitive behavior,^[16,34–36] and most likely arises from the successive movement of electrons into the unoccupied molecular orbitals. Furthermore, the dQ/dV plots reveal subtle potential peaks implying multiple-electron transfer during discharge (Figure 2d).

The cycling and rate performance of cell 1 were further evaluated (Figure 3a). Notably, the discharge capacity gradually increased after 10 cycles and was maintained at approximately 186 mAhg⁻¹, with a coulombic efficiency of 84% after the 20th cycle at 200 mA g^{-1} (Figure 3a). This result implies that the original CuDEPP electrode was electrochemically altered in initial cycles, as observed by CV. Our studies confirmed that the initial charging process is beneficial for cell 1 to achieve a high capacity and stable cycling behavior and thus can be considered as a "selfconditioning" process. Discharge capacities of 163, 143, 132, and 125 $mAh\,g^{-1}$ (corresponding to average capacitances of 216, 190, 175, 166 F g⁻¹, respectively) were retained at 1, 2, 4, and 6 Ag^{-1} , respectively, within 100 cycles. The discharge capacities were mostly restored when the current was tuned from 10 to 1 Ag^{-1} , which demonstrates excellent rate capability. The selected discharge curves in Figure 3b show only slightly decreased potentials with increasing current and cycle. Remarkably, even at a high current of 10 Ag^{-1} (53 C), the electrode could still deliver a capacity of 115 mAhg⁻¹ (153 Fg^{-1}) within 42 s with a coulombic efficiency of 99%. These values correspond to a specific energy density of 345 Whkg⁻¹ and a specific power of 29 kWkg⁻¹. The outstanding cycling stability of the cell at an extremely high current is also shown by the characteristic charge/discharge profiles, in which the voltage curves are virtually unchanged over 100 cycles (see Figure S16).





Figure 3. a) Rate capability. b) Discharge curves. c) Cycling performance. d) Charge/discharge profiles.

The long-term cycling performance was also studied at 4 A g^{-1} (21 C; Figure 3c). The cell was initially operated for 20 cycles at 200 mA g^{-1} for "self-conditioning". A maximum capacity of 150 mAh g^{-1} (200 F g^{-1}) was observed in the 226th cycle, and the capacity retention was about 85% for the first 2000 cycles and 60% after 8000 cycles with a coulombic efficiency close to 100%. Accordingly, a specific energy density of 240 Wh kg⁻¹ at a power density of 11 kW kg⁻¹ was observed with a cycle life of more than 8000 cycles. Selected charge/discharge curves indicate a stable capacity with an average discharge voltage of 3 V (Figure 3d). Additional CVs, in which overlapping curves and well-defined redox peaks at about 3 V were visible, were recorded after the cell was cycled 2000 times at a current of 4 Ag^{-1} (see Figure S17), which further supports the high power capability of the electrode.

To gain more insight into the mechanism of the beneficial "self-conditioning" process for cell 1, we carried out postmortem analysis. The cycled electrode material had an even lower solubility in organic solvents than the initial CuDEPP, which impeded some characterization techniques. On the other hand, the lower solubility reflects the chemical change of the material by the electrochemical reactions. The morphology and crystallinity of CuDEPP after the first cycles was analyzed by exsitu SEM and XRD. The rod shape of CuDEPP remained unchanged after 10 cycles (see Figure S18). However, the crystallinity was reduced after the 1st charge and further lowered in the discharged state as shown by XRD (see Figure S19). This reduced crystallinity can be ascribed to the decrease in the long-range order of the crystals by possible chemical changes during the first charging and the progressive incorporation of PF_6^- and Li^+ into the lattice of CuDEPP in subsequent cycles.^[37] The insertion/ deinsertion of PF_6^- in the electrode is also supported by ex situ IR spectroscopy, in which signals at 838 and 556 cm⁻¹ for PF_6^- appeared after charging and disappeared after discharging of the cell (Figure 4a). The vanishing of the C–H stretching band at 3264 cm⁻¹, which is characteristic for the ethynyl group, after the 1st charge provides clear evidence of a change in the -C=C-H moiety of CuDEPP (see Figure S20).

In the light of studies on the electrochemically assisted attachment of a porphyrin to the electrode surface through ethynyl linkages^[38,39] and the electrochemical-oxidationinduced polymerization of functionalized porphyrins.[40-43] we propose that the CuDEPP molecules could be immobilized on the electrode and/or undergo electrochemical polymerization to link ethynyl groups. This hypothesis is further supported by the HOMO values of the CuDEPP monomer and dimer (0.28 eV higher than that of the monomer), as increasing polymer lengths correlate to decreasing LUMO and increasing HOMO energies (see Figure S21). The small LUMO-HOMO gap in the polymerized molecule is consistent with the enhanced electrical conductivity of the material. The charge-transfer resistance of the CuDEPP electrode was significantly reduced after the initial cycling (see Figure S22), thus strongly supporting the enhanced electrical conductivity after self-conditioning. An extended mechanistic study is undergoing.

To further explore the bipolar reactivity of CuDEPP, we configured a lithium-free system as cell 2 (Figure 1 d). CV was performed with graphite as the working electrode and CuDEPP as the counterelectrode in PP14TFSI (see Figure S23). In the first anodic sweep, a pair of redox peaks



Figure 4. a) IR spectra of the CuDEPP cathode in cell 1. b) Cycling performance of cell 2. c) Charge/discharge profiles of cell 2. d) XRD patterns of the graphite cathode.

associated with the intercalation/deintercalation of TFSI⁻ anions into/from the graphite presented at 3.51/3.14 V.^[44,45] Three additional reduction peaks at 2.57, 1.73, and 0.66 V in the first cathodic sweep indicate a multistage deintercalation of TFSI⁻ anions.^[44,45] The galvanostatic tests for cell 2 were carried out at an operating voltage between 4.0 and 0.0 V. An initial discharge capacity of 94 mAhg⁻¹ was observed at 1 Ag⁻¹ (see Figure S24), which is close to the theoretical value based on two-electron transfer (CuDEPP→CuDEPP²⁻, 93.5 mAhg⁻¹). When the cycling performance was tested at 5 Ag⁻¹ (53 C), a reversible discharge capacity of 44 mAh g⁻¹ was retained after 200 cycles (Figure 4b). Selected charge/ discharge curves show an average cell potential around 2.0 V with stable cyclability at 53 C (Figure 4c), thus implying a high power density of the cell. Good rate capability was demonstrated at a current from 1 to 10 Ag⁻¹ (see Figure S24). Notably, a discharge capacity of 32 mAhg⁻¹ was obtained within 12 s at 10 Ag⁻¹ (106 C), corresponding to a specific power of 14 kWkg⁻¹.

The reversible intercalation of TFSI⁻ anions into the graphite layers was verified by means of SEM, EDX, and XRD (see Figure S25). The XRD patterns (Figure 4d) of the charged graphite indicate that the characteristic 002 diffraction peak ($2\theta = 26.4^{\circ}$) of graphite shifted to a lower diffraction angle ($2\theta = 25.3^{\circ}$), thus indicating a lattice expansion, and almost returned to its original position after discharge.

In summary, the porphyrin CuDEPP is a highly promising electrode material in various battery systems. In contrast to the slow discharge/charge processes in conventional LIBs, the CuDEPP electrode exhibits a rapid redox conversion involving the transfer of up to four electrons. In a lithium-based cell, a CuDEPP electrode could deliver an initial capacity of 210 mAh g^{-1} . The cell could be operated more than 8000 times at high currents with good capacity retention. Stable capacity and high energy density at a high specific power have been demonstrated. Furthermore, CuDEPP could be used as an anode in a lithium-free cell with good cyclability and rate capability. Unlike common organic electrodes, the redox activity of the CuDEPP molecule is based on its relevant mesomeric structures, and the ethynyl groups improve battery performance. The multifunctional electrode material CuDEPP and its outstanding properties open up new pathways for the design of organic electrode materials.

Acknowledgements

This study was supported by the China Scholarship Council (CSC) and the MagS project (3XP0032E) of the German Ministry of Research and Education (BMBF). We acknowledge the Karlsruhe Nano Micro Facility (KNMF, www.kit. edu/knmf) for provision of access to instruments at their laboratories.

Conflict of interest

The authors declare no conflict of interest.

Keywords: energy storage \cdot materials science \cdot porphyrinoids \cdot rechargeable batteries \cdot self-conditioning electrodes

How to cite: Angew. Chem. Int. Ed. 2017, 56, 10341–10346 Angew. Chem. 2017, 129, 10477–10482

 N. S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y. K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, *Angew. Chem. Int. Ed.* 2012, *51*, 9994; *Angew. Chem.* 2012, *124*, 10134.





- [2] H. D. Yoo, E. Markevich, G. Salitra, D. Sharon, D. Aurbach, *Mater. Today* 2014, 17, 110.
- [3] A. Manthiram, J. Phys. Chem. Lett. 2011, 2, 176.
- [4] J.-M. Tarascon, M. Armand, Nature 2001, 414, 359.
- [5] J. B. Goodenough, K.-S. S. Park, J. Am. Chem. Soc. 2013, 135, 1167.
- [6] P. Simon, Y. Gogotsi, Nat. Mater. 2008, 7, 845.
- [7] G. P. Wang, L. Zhang, J. J. Zhang, *Chem. Soc. Rev.* 2012, *41*, 797.
 [8] K. Naoi, S. Ishimoto, J. Miyamoto, W. Naoi, *Energy Environ. Sci.* 2012, *5*, 9363.
- [9] D. Larcher, J.-M. Tarascon, Nat. Chem. 2015, 7, 19.
- [10] K. Sakaushi, E. Hosono, G. Nickerl, T. Gemming, H. Zhou, S. Kaskel, J. Eckert, *Nat. Commun.* 2013, *4*, 1485.
- [11] Y. Liang, Z. Tao, J. Chen, Adv. Energy Mater. 2012, 2, 742.
- [12] Z. Song, H. Zhou, *Energy Environ. Sci.* **2013**, *6*, 2280.
- [13] Z. Song, Y. Qian, T. Zhang, M. Otani, H. Zhou, Adv. Sci. 2015, 2, 1500124.
- [14] T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager, U. S. Schubert, *Nature* 2015, 527, 78.
- [15] V. Gupta, N. Miura, Electrochim. Acta 2006, 52, 1721.
- [16] J. Y. Shin, T. Yamada, H. Yoshikawa, K. Awaga, H. Shinokubo, *Angew. Chem. Int. Ed.* **2014**, *53*, 3096; *Angew. Chem.* **2014**, *126*, 3160.
- [17] L. R. Milgrom, The Colors of Life: An Introduction to the Chemistry of Porphyrins and Related Compounds, Oxford University Press, Oxford, 1997.
- [18] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **2011**, *334*, 629.
- [19] D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 2009, 42, 1890.
- [20] G. F. Swiegers, D. R. MacFarlane, D. L. Officer, A. Ballantyne, D. Boskovic, J. Chen, G. C. Dismukes, G. P. Gardner, R. K. Hocking, P. F. Smith, L. Spiccia, P. Wagner, G. G. Wallace, B. Winther-Jensen, O. Winther-Jensen, *Aust. J. Chem.* **2012**, *65*, 577.
- [21] T. Kakui, S. Sugawara, Y. Hirata, S. Kojima, Y. Yamamoto, *Chem. Eur. J.* 2011, 17, 7768.
- [22] C. Liu, D. Shen, Q. Chen, J. Am. Chem. Soc. 2007, 129, 5814.
- [23] Y. Yamamoto, A. Yamamoto, S. Furuta, M. Horie, M. Kodama, W. Sato, K. Akiba, S. Tsuzuki, T. Uchimaru, D. Hashizume, F. Iwasaki, J. Am. Chem. Soc. 2005, 127, 14540.
- [24] M. Liao, S. Scheiner, J. Chem. Phys. 2002, 117, 205.
- [25] 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.
- [26] H. Zhang, Y. Zhang, C. Gu, Y. Ma, Adv. Energy Mater. 2015, 5, 1.

- [27] F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu, Angew. Chem. Int. Ed. 2015, 54, 6814; Angew. Chem. 2015, 127, 6918.
- [28] The Porphyrin Handbook (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, 2003.
- [29] S. Prathapan, T. E. Johnson, J. S. Lindsey, J. Am. Chem. Soc. 1993, 115, 7519.
- [30] R. Stranger, J. E. McGrady, D. P. Arnold, I. Lane, G. A. Heath, *Inorg. Chem.* **1996**, *35*, 7791.
- [31] V. S. Lin, S. G. Dimagno, M. J. Therien, *Science* 1994, 264, 1105.
 [32] H. L. Anderson, S. J. Martin, D. D. C. Bradley, *Angew. Chem.*
- *Int. Ed. Engl.* **1994**, *33*, 655; *Angew. Chem.* **1994**, *106*, 711. [33] M. Inamo, H. Kumagai, U. Harada, S. Itoh, S. Iwatsuki, K.
- Ishihara, H. D. Takagi, *Dittor Trans.* **2004**, 1703.
- [34] J. C. Bachman, R. Kavian, D. J. Graham, D. Y. Kim, S. Noda, D. G. Nocera, Y. Shao-Horn, S. W. Lee, *Nat. Commun.* 2015, 6, 7040.
- [35] P. Jiménez, E. Levillain, O. Alévêque, D. Guyomard, B. Lestriez, J. Gaubicher, Angew. Chem. Int. Ed. 2017, 56, 1553; Angew. Chem. 2017, 129, 1575.
- [36] T. Liu, K. C. Kim, B. Lee, Z. Chen, S. Noda, S. S. Jang, S. W. Lee, *Energy Environ. Sci.* 2016, 10, 205.
- [37] Z. Zhang, H. Yoshikawa, K. Awaga, Chem. Mater. 2016, 28, 1298.
- [38] M. V. Sheridan, K. Lam, W. E. Geiger, J. Am. Chem. Soc. 2013, 135, 2939.
- [39] M. V. Sheridan, K. Lam, W. E. Geiger, Angew. Chem. Int. Ed. 2013, 52, 12897; Angew. Chem. 2013, 125, 13135.
- [40] F. Bedioui, J. Devynck, C. Bied-Charreton, Acc. Chem. Res. 1995, 28, 30.
- [41] K. A. Macor, T. G. Spiro, J. Am. Chem. Soc. 1983, 105, 5601.
- [42] A. Bettelheim, B. A. White, S. A. Raybuck, R. W. Murray, *Inorg. Chem.* 1987, 26, 1009.
- [43] Y. Q. Zhang, N. Kepčija, M. Kleinschrodt, K. Diller, S. Fischer, A. C. Papageorgiou, F. Allegretti, J. Björk, S. Klyatskaya, F. Klappenberger, M. Ruben, J. V. Barth, *Nat. Commun.* 2012, 3, 1286.
- [44] S. Rothermel, P. Meister, G. Schmuelling, O. Fromm, H.-W. Meyer, S. Nowak, M. Winter, T. Placke, *Energy Environ. Sci.* 2014, 7, 3412.
- [45] T. Placke, S. Rothermel, O. Fromm, P. Meister, S. F. Lux, J. Huesker, H.-W. Meyer, M. Winter, J. Electrochem. Soc. 2013, 160, A1979.

Manuscript received: March 17, 2017

- Revised manuscript received: May 16, 2017
- Accepted manuscript online: June 19, 2017
- Version of record online: July 19, 2017