Zampardi, Giorgia ; La Mantia, Fabio

Prussian blue analogues as aqueous Zn-ion batteries electrodes: Current challenges and future perspectives

Journal Article as: peer-reviewed accepted version (Postprint)
DOI of this document*(secondary publication): https://doi.org/10.26092/elib/3657
Publication date of this document: 14/02/2025

* for better findability or for reliable citation

Recommended Citation (primary publication/Version of Record) incl. DOI:

Giorgia Zampardi, Fabio La Mantia,
Prussian blue analogues as aqueous Zn-ion batteries electrodes: Current challenges and future perspectives,
Current Opinion in Electrochemistry, Volume 21, 2020, Pages 84-92,
ISSN 2451-9103, https://doi.org/10.1016/j.coelec.2020.01.014.

Prussian blue analogues as aqueous Zn-ion batteries electrodes: Current challenges and future perspectives

Giorgia Zampardi and Fabio La Mantia

Abstract

The urgency of integrating renewable energy sources in the power grid has pushed the development of aqueous metal-ion batteries because of their low cost, nontoxicity, high safety, and environmentally friendliness. Among the variety of aqueous metal-ion batteries that are currently under development, aqueous Zn-ion batteries (A-ZIBs) have recently gained a great attention because of their high specific energy and high reversibility in aqueous solutions, together with the low cost and high abundancy of the zinc. In this article, the authors intend to present an overview of the Prussian blue analogue materials, which are among the most promising materials for positive electrodes in A-ZIBs because of their easier synthesis route, reversible ion-insertion, high safety, and low toxicity, highlighting their strength points and open challenges.

Addresses
Universität Bremen, Energiespeicher- und Energiewandlersysteme,
Bibliothekstraße 1, 28359 Bremen, Germany

Corresponding authors: La Mantia, Fabio (lamantia@uni-bremen.de);
Zampardi, Giorgia (zampardi@uni-bremen.de)

Keywords
Aqueous Zn-ion batteries (A-ZIBs), Cathodes materials, Copper hexacyanoferrate (CuHCF), Hexacyanoferrates (HCF), Zn-ion insertion, Hexacyanometallates, Metal hexacyanoferrates (MHCFs), Prussian blue analogues (PBAs), Prussian blue derivative, Zinc hexacyanoferrate (ZnHCF), Zinc-ion intercalation.

Introduction

To meet the energy needs that are nowadays required by our society, technologies employing renewable energy sources, such as wind and sun are under development and optimization [1–6]. In the majority of the cases, an accumulation step is required before letting the harvested electrical energy into the power grid, often through the employment of batteries [4,7–9]. For this reason, batteries for large-scale stationary applications are under current development [7]. Such batteries do not need stringent requirements in terms of energy- and power-density; however, they need to be environmentally friendly, safe, and cost-effective. Therefore, battery systems operating in an aqueous environment are to be preferred over the organic-based ones. Researchers are currently developing aqueous metal-ion batteries that are based on monovalent (Li^+, Na^+, K^+) and divalent (Zn^{2+}, Mg^{2+}, etc.) cations. Among these, aqueous Zn-ion batteries (A-ZIBs) have recently gained a great attention because of their high specific power and high reversibility in aqueous solutions, together with the low cost and high abundancy of the zinc [10–12].

The negative electrode of an A-ZIB is usually constituted of metallic Zn as foil [13], as deposit on a substrate [14], or as a Zn-powder containing composite electrode [15–17]. At the negative electrode, Zn^{2+} ions are electrodeposited and dissolved during the cycling of the battery. The electrodeposition reaction may occur not homogeneously, thus leading to the formation of metallic zinc dendrites, which may grow through the separator, short-circuiting the electrodes. Despite the dendrite formation is a major issue that needs further optimization when the Zn electrodeposition occurs in alkaline media, it is almost negligible in neutral and slightly acidic solutions [18]. Moreover, the use of high surface area and nanostructured Zn-based electrodes can help reducing the dendrite formation on Zn-deposition [8,19,20]. The major limitation that needs to be overcome on the Zn negative electrode side is the hydrogen evolution reaction taking place at the potentials where Zn is electrodeposited, leading to a lower cycling efficiency, a reduced calendar life of the battery, and higher safety hazard related to the overpressure built inside the ZIB [15,17]. For this reason, electrolytes having acidic pH should be avoided, since they promote the formation of H_2 [21,22]. Recently, researchers have been using additives in solution [15], as well as solid-state additives within the electrode itself [23], to slow down the hydrogen evolution at the Zn-based electrodes.

Despite the challenges related to the negative electrode, what hinders the commercialization of A-ZIBs is finding a suitable, cheap, and environmentally friendly Zn^{2+} insertion material having high capacity and stability during cycling [15,23]. Different classes of materials are currently under investigation as potential positive electrodes for A-ZIBs, such as manganese oxides [24–27], vanadium oxides and vanadium oxide derivatives [10,11,28–30], and Prussian blue analogues (PBAs) [12,31–33]. A-ZIBs based on manganese oxide were shown to reach a good cycle life [24–26]. However, these electrodes suffer from an intrinsically low ionic and electronic conductivity, a relatively low reversibility, and a sharp initial capacity fading in aqueous solutions [24–27]. Vanadium-based electrodes have been shown to reach promising capacities and cycle life, especially at high current rates [10,11,28–30]. However, vanadium-based compounds have usually a low operating potential [10,11,28–30], leading to low energy density of the final battery and, in some cases, they are supposed to insert H^+ together with Zn^{2+} in their structure, lowering the Coulombic efficiency [28,30]. Moreover, they may be toxic and environmentally unfriendly, and they require nonstraightforward synthesis procedures to obtain the desired stoichiometry and crystallographic structure [10,11,28–30].

In this article, the authors will focus on PBAs that are currently under development as positive electrodes in ZIBs, highlighting their strength points and open challenges (Figure 1).

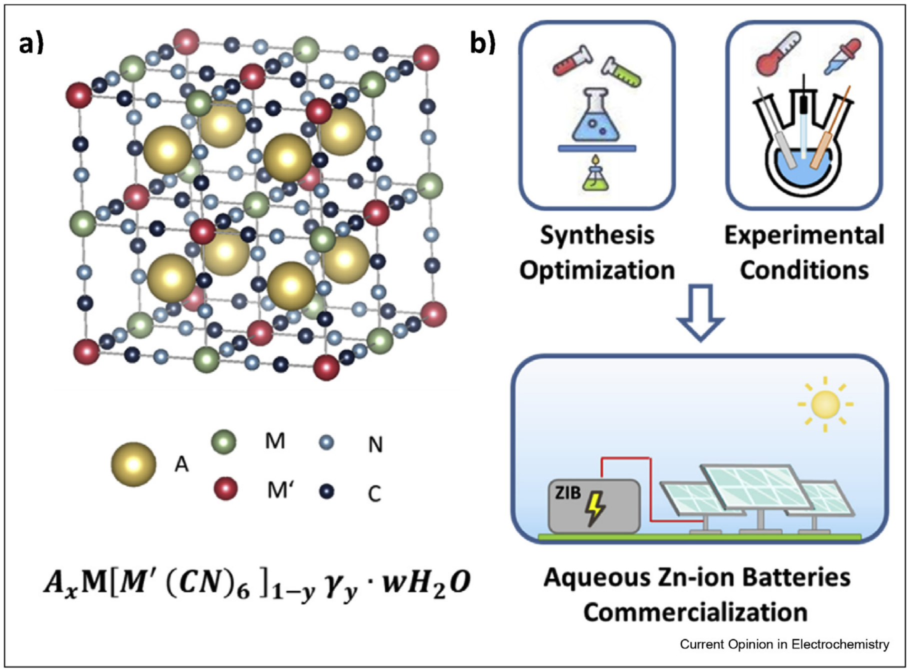
Prussian blue analogues

The main reasons hindering the commercialization of A-ZIBs are related to their low energy and power density and, most importantly, short cycle life and costs still too high for these storage systems to be competitive with lithium-ion batteries for stationary applications. These disadvantages are strongly related to the active material at the positive electrode. Manganese oxide–based A-ZIBs are characterized by low costs but short cycle life and low power densities. On the other side, vanadium-based A-ZIBs show long cycle life, high energy density but high costs, low environmentally friendliness, and difficulties in the industrial scale-up of the material's synthesis.

As we will discuss in this section, PBAs, despite not standing out in terms of cycle life or energy density, show an excellent compromise in terms of average cycle life, extremely low costs, and excellent power density, together with an intrinsic easy synthesis route that can be easily scaled up at an industrial level. All these characteristics make PBAs a realistic option as positive electrode materials for commercializing A-ZIBs.

Hexacyanometallates, often referred to as PBAs, are materials constituted by an open framework

Figure 1



Current Opinion in Electrochemistry

Structure and optimization strategies of Prussian blue analogues. **(a)** Schematic representation of the crystal structure of the class of materials belonging to the Prussian blue analogues (PBAs); **(b)** schematic representation of the parameters to optimize to commercialize aqueous Zn-ion batteries based on PBAs.

face-centered cubic lattice, having an *fm3m* space group. The nominal formula of this class of materials can be written as:

$$A_x\mathrm{M}[M(CN)_6]_{1-y}\gamma_y \bullet wH_2O$$

where, A is the alkaline cation, M and M′ the transition metals coordinated octahedrally to the nitrogen atoms and the carbon atoms of the cyanide group, respectively, and γ the hexacyanometallate complex vacancy (the primer defect of such crystallographic structure) [34]. As schematically represented in Figure 1a, each unit cell consists of eight subunits (i.e. interstitial sites/subcells) that are able to accommodate neutral species and/or cations. PBA crystal structures are characterized by large interstitial sites, often called 'A sites', and large channels in the 100 directions, which are responsible for the high solid diffusion coefficient (10^{-9} to 10^{-8} cm^2 s^{-1}) and ionic conductivity of this class of materials [34–38]. As a consequence, different PBAs having different transition metals in their lattice can reversibly (de-)insert a variety of monovalent (e.g. Na^+, Li^+, K^+, etc.), divalent (e.g. Zn^{2+}, Mg^{2+}, Ca^{2+}, etc.), and trivalent cations (e.g. Al^{3+}) [34,35,37–46]. PBAs can accommodate two types of water molecules within their structure as well: (1) zeolitic water, in the octahedral center of the subcells and (2) water coordinated with the M transition metal [42,47]. In particular, it has been suggested that zeolitic water may facilitate the ion insertion process within PBAs through shielding the charge of the inserted ion, thus reducing the electrostatic forces between the inserted ion and the host material [42,47].

In the last decade, PBAs have attracted a great attention as promising electrode materials for metal-ion battery applications because they offer the following advantages [34–38,46,48–50]:

- Easy and inexpensive synthesis procedure
- High specific capacity for the reversible insertion of a variety of metallic ions
- High ionic conduction within their crystal structure
- Electrochemical properties that can be tuned through the variation of the material composition
- Minimal volume changes during the ion (de-)insertion process
- High safety and nontoxicity
- Environmental friendliness

Different materials belonging to the PBA family are promising candidates mainly as positive electrodes in a variety of metal-ion battery applications: from organic-based Na-, K-, and Zn-ion to aqueous Li-, Na-, K-, Zn-, Mg-, Al-, Ca-ion batteries [34–38,44–46]. In the following sections, the authors will focus their attention on PBAs that are most promising for A-ZIB applications.

Iron Hexacyanoferrate—Prussian blue

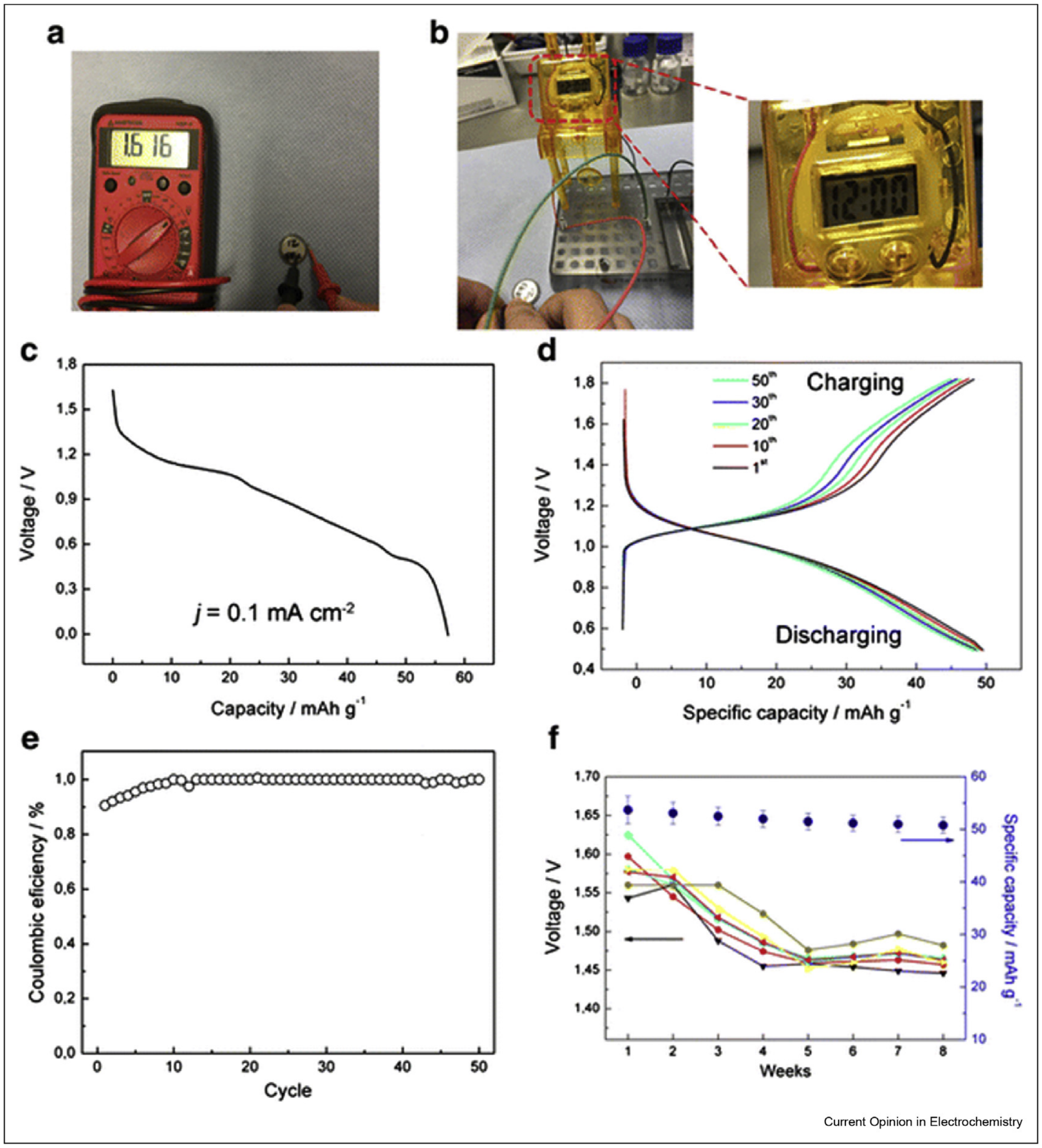
Prussian blue (PB), i.e. iron(III) hexacyanoferrate (II) (HCF), is the predecessor of the hexacyanometallates family, being used since more than a century as a pigment for paints and even as a remedy against a variety of heavy metal poisoning [16,51]. Considering the highly reversible insertion kinetics of K^+ ions from aqueous-based solutions at room temperature, PB-based electrodes are under development as insertion materials for K-ion batteries [44,45]. Recently, PB has been proposed as insertion material for the positive electrodes in ZIBs as well [16,31,52]. In 2016 Zhen et al. demonstrated that highly crystalline PB nanocubes (c.a. 150 nm) underwent a reversible Zn^{+2} (de-)insertion, with a capacity of c.a. 120 mAh g^{-1} [31]. As solution the authors employed a mixture of choline acetate ionic liquid and water (70 : 30 %vol.), containing zinc acetate as salt. Being choline acetate a biodegradable derivate of vitamin B4, the electrolyte employed was nontoxic, and it allowed a good Coulombic efficiency of the PB-based electrode at 0.1C, in flooded half-cell tests [31]. Later, the same authors built a prototype battery constituted of PB nanocubes and metallic zinc, using the same electrolytic solution [16]. With its nominal voltage of 1.6 V and a capacity of c.a. 54 mAh g^{-1}, the battery was able to power a digital clock (Figure 2). Despite the proposed ionic liquid fulfils the requirement of nontoxicity and allows a reversible Zn^{+2} (de-)insertion within the PB, the system needs to be further optimized to reduce the rapid capacity fading observed with increasing current density, due to Zn^{+2} diffusion limitations in the electrolyte [16,31].

Moreover, PB-based electrodes have been recently proposed as a promising alternative for the positive electrodes in hybrid aqueous Na-ion/A-ZIB [52]. Due to the structural stability of the PB electrode, half-cell measurements reported a good capacity of c.a. 75 mAh g^{-1}, and a good cycle life [52].

Zinc hexacyanoferrate

Zinc hexacyanoferrate (ZnHCF) can be employed as an insertion material for K^+, Na^+, and Zn^{2+}-based batteries [53,54]. It has been shown that the discharge capacity and the electrochemical cycling of the material in Zn-containing aqueous electrolytes are strongly influenced by the particles' morphology. Namely, cuboctahedral particles show a higher discharge capacity of c.a. 70 mAh g^{-1}, compared to truncated octahedral and octahedral ones [32]. It has been suggested that in the case of the cuboctahedral particles there may be a better diffusion of the Zn^{2+} ions probably correlated to the shape and orientation of the surface of the ZnHCF particles [32]. Different particle shapes and morphologies can be obtained with the coprecipitation method (Figure 3), through controlling some synthesis parameters such as the dropping speed [32,53] and the reactants concentration [32,53,55].

Figure 2

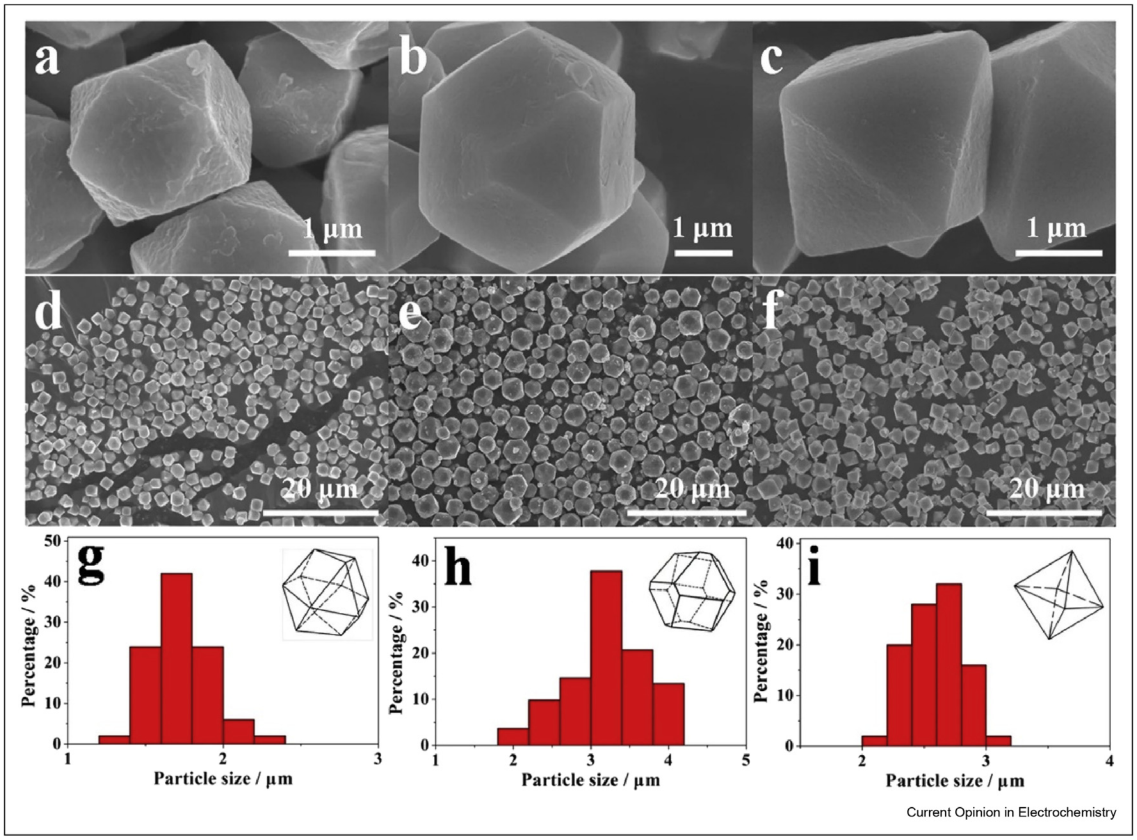


Current Opinion in Electrochemistry

Prussian blue/zinc coin cell. (a), **(b)** Photographs of the freshly prepared Zn/PBA button cell and its application in a digital clock; **(c)** voltage profile during discharging at a current density of 0.1 mA cm^{-2}; **(d)** galvanostatic charge and discharge curves of the cell between +1.8 and + 0.5 V at a current density of 0.1 mA cm^{-2}; **(e)** Coulombic efficiency of the cell; and **(f)** self-discharge test by measuring the potential and specific capacity of the cell over 8 weeks. Reprinted from Ref. [16], copyright (2017), with permission from Springer.

Moreover, SEM analysis suggested that also the removal of the coordinated water through thermal treatment can lead to a modification of the material structure from cubic to rhombohedral, causing a change in the N—Zn—N bond angle [32]. In this case, the electrochemical properties of the resulting rhombohedral ZnHCF were less appealing than the ones of the material having a cubic structure [32,53]. Recently, a full cell was built having a positive electrode constituted of rhombohedral ZnHCF particles and a Zn-ion insertion material based on molybdenum as a negative electrode, delivering an overall discharge capacity of c.a. 60 mAh g^{-1}, and a full cell voltage of c.a. 1.4 V [56]. Even though it has to be considered that the ZnHCF needs further optimization to reach higher energy density and especially cycle life, and that an insertion material based on molybdenum is not advised for A-ZIBs due to its high cost, this proof-of-concept demonstrated the feasibility of aqueous rocking-chair ZIBs.

Figure 3



Different ZnHCF morphologies. SEM images of **(a,d)** cuboctahedron ZnHCF, **(b,e)** truncated octahedron ZnHCF, and **(c,f)** octahedron ZnHCF obtained at room temperature, and their size distribution histograms **(g)** for cuboctahedron ZnHCF, **(h)** for truncated octahedron ZnHCF, and **(i)** for octahedron ZnHCF, respectively) plotted by counting 50 random particles. Reprinted from Ref. [32].

Copper hexacyanoferrate

Copper hexacyanoferrate (CuHCF) has been for the first time proposed as a positive electrode for A-ZIBs contemporaneously by Jia et al. and by Trocoli et al., in 2015. In their proof-of-concept work, Jia et al. showed the reversible Zn^{2+} (de-)insertion in the first 20 cycles of a paste electrode based on CuHCF nanoparticles in an aqueous solution containing 1 M $ZnSO_4$ [57]. At the same time, Trocoli et al. reported in their seminal work the reversible Zn^{2+} (de-)insertion in CuHCF during the first 100 cycles performed at a current rate of 1C in a 20 mM $ZnSO_4$ aqueous solution [12]. The capacity retention of CuHCF was reported to be 77% after 20 cycles in 1 M $ZnSO_4$ [57], and 96.3% after 100 cycles in 20 mM $ZnSO_4$ [12], respectively. Moreover, the overall voltage of a full cell constituted of CuHCF/Zn^0 was reported to be 1.73 V, a value that remains one of the highest reached for A-ZIBs based not only on PBAs but also on vanadium and manganese compounds [10–12,28–30].

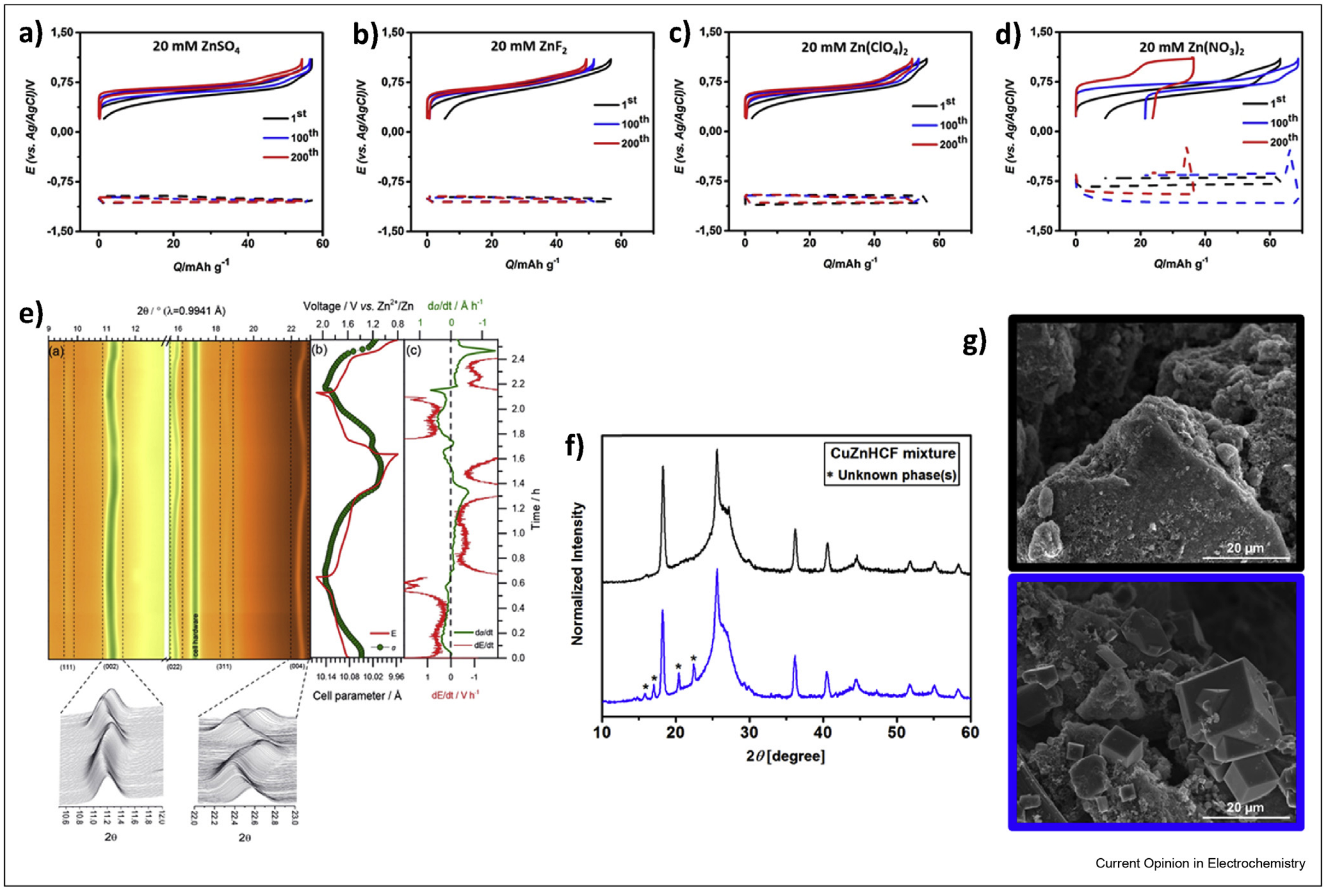
From that moment on, CuHCF attracted a great attention as positive electrode material for A-ZIBs, thanks to its relatively high operating potential, leading to a competitive energy density of the overall Zn-ion cell [12], its excellent performance at different charging speeds [12], making CuHCF ideal for stationary grid applications, its easy and inexpensive synthesis route, and its nontoxicity. Despite CuHCF is one of the most promising materials within the PBA family for ZIB applications, its relatively fast aging presently limits its use in real-life systems. For this reason, most of the research efforts is currently directed toward investigating the aging mechanism of CuHCF, which has been proven not trivial to be assessed, and therefore not yet fully understood.

Detailed electrochemical studies performed by Kasiri et al. clearly showed a variation in the Zn^{2+} (de-)insertion mechanism, which changes from an initial single-phase one to a two-phase one, leading to a severe capacity fading of the material [58]. ICP-MS analysis demonstrated that no Cu atoms were found in the electrolyte; therefore, such transition in the insertion mechanism does not provoke any CuHCF dissolution, but rather the material changes its structure and/or its composition on cycling [58]. It has been shown that the moment when such (de-)insertion mechanism change occurs in the CuHCF depends not only on the nature of the anion but also on the concentration of Zn^{2+} in the aqueous electrolyte and on the current C-rate [58] (Figure 4a–d). Namely, it occurred at a later stage in SO_4^{2-} and ClO_4^--based solutions (compared to F^- and NO_3^--based ones), and at an earlier stage with increasing concentration of Zn^{2+}, and decreasing the C-rate [58]. The authors suggested that such change in the Zn (de)-insertion mechanism may occur once the CuHCF reaches a determined state of charge, or it may have a prevalent chemical nature [58].

To explain the capacity fading of the material, the authors proposed that on continuous Zn insertion, the CuHCF crystal structure is distorted because of an exchange of Zn ions in the material's lattice, thus leading to the formation of a new phase. Since only a negligible amount of Cu^{2+} was found in solution after the CuHCF was cycled, the authors argued that instead of substituting the Cu atoms in the CuHCF lattice, the Zn ions are incorporated within the lattice's vacancies [58]. Later operando synchrotron X-ray diffraction studies performed by Renman et al. also confirmed that Zn^{2+} may be allocated within the vacancies of the CuHCF crystal structure, since a nonlinear expansion/contraction of the unit cell parameter was observed during the initial Zn^{2+} insertion/deinsertion [59] (Figure 4e).

A recent postmortem study of the morphology of CuHCF based on electron microscopy techniques performed by Lim et al. suggested that the Zn irreversibly inserted within the CuHCF lattice on long-

Figure 4



Effect of the electrolyte on the aging of CuHCF. (a–d) Potential profile of CuHCF (solid line) and Zn foil (dashed line) at 1C current rate in 20 mM $ZnSO_4$, $Zn(ClO_4)_2$, ZnF_2, and $Zn(NO_3)_2$ aqueous solutions, respectively. Reprinted from Ref. [58] copyright (2016), with permission from Elsevier; **(e)** *(a)* Top-view elevation map displaying peak shifts of a CuHCF/Zn cell during the in operando XRD experiment, *(b)* time evolution of the corresponding voltage profile (continuous line) of the first two cycles with the refined lattice parameter (circles) superimposed. *(c)* A plot of the time-derivative of both the voltage (dE/dt) and the cell parameter (da/dt). Reprinted from Ref. [59], copyright (2017), with permission from Elsevier; **(f)** XRD patterns of CuZnHCF (93:7) electrode before cycling (black) and after 1000 cycles (blue) at 1C rate in 20 mM $ZnSO_4$; **(g)** SEM images of CuZnHCF (93:7) electrode before (black) and after (blue) 1000 cycles in 20 mM $ZnSO_4$. Reprinted from Ref. [33], copyright (2019), with permission from Elsevier.

term cycling may be found not only within the lattice vacancies but also within the crystal structure itself, taking the place of the Cu atoms, and leading to the formation of $Cu(CN)_2$ and $CuZn(CN)_4$ [60]. Containing such morphologies no Fe^{2+}/Fe^{3+}, the authors suggested them to be electrochemically inactive, thus contributing to the capacity fading of the material.

Attempts to identify the exact structure of the newly formed phase during the CuHCF aging have been made through XRD studies. However, since it was not possible to clearly identify the newly formed phase, the authors suggested that this was a distorted one, probably a mixture of CuHCF and ZnHCF [61].

Therefore, Kasiri et al. synthesized a variety of mixed zinc—copper hexacyanoferrates (CuZnHCF) with different Zn:Cu ratios, to have a better control of the content of Zn within the lattice, both substituting the Cu atoms and within the vacancies. Among the different CuZnHCFs, the one with Zn:Cu of 7:93 showed a better capacity retention compared to the pure CuHCF: namely, 85.5% against 74% after 1000 cycles in 20 mM $ZnSO_4$ for CuZnHCF and CuHCf, respectively [33]. By performing a thorough electrochemical and morphological postmortem analysis, the authors ascribed such better performance of the CuZnHCF mixture to the formation of more crystalline morphologies during the material aging. In this case, the different morphologies observed through postmortem analysis were both cubic and noncubic, having at least two compositions, mostly Zn-rich and Fe-rich [33] (Figure 4f and g). Since the CuZnHCF mixture delivered an encouraging 11% more charge capacity and 11% more energy compared to the pure CuHCF, the authors pointed out that an optimization of the crystal structure of the CuHCF-based material may effectively postpone its degradation mechanism.

Conclusions and perspectives

The intrinsic nontoxicity, high reversibility, and environmentally friendliness characterizing the family of PBAs make them ideal candidates as active materials for the positive electrodes of A-ZIBs. Moreover, their easy synthesis procedure is extremely appealing for their possible scaled-up production, in view of a commercialization of aqueous Zn-ion cells.

What currently hinders the commercialization of aqueous zinc-ion batteries is related to their short cycle life and high costs, making other alternatives that are already available within the market (such as Li-ion batteries in terms of cycle life, and lead—acid batteries in terms of low costs) more appealing. In view of their low costs, low toxicity, and good power density, PBAs may realistically promote the commercialization of A-ZIBs for stationary storage applications, provided that an improvement of their cycle life is achieved. Among the great variety of PBAs, the most promising one for this application currently appears to be the CuHCF and its mixtures. However, also in this case the main limitation to the commercialization of A-ZIBs based on CuHCF remains their short cycle life. For this reason, research efforts should be directed toward the understanding of the PBAs' aging mechanism, in particular focusing on a possible correlation between the defects of the crystal structure and the cycle life.

Other aspects requiring a more thorough investigation are related to the effect of the experimental conditions (such as electrolyte composition, additives and temperature), together with the effect of the change of the substituting transition metal atoms in the crystallographic lattice on the materials' aging.

We believe that a deeper understanding of the mechanism of the Zn (de-)insertion reaction and of the aging processes occurring within PBA-based electrodes will lead to their optimization, which can be achieved through a careful control of the synthesis parameters and of the experimental conditions, thus promoting the commercialization of cheap and green aqueous zinc-ion batteries.

Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Acknowledgements

The financial support of the Federal Ministry of Education and Research (BMBF) in the framework of the project 'ZIB' (FKZ 03XP0204A) is gratefully acknowledged.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Delucchi MA, Jacobson MZ: **Providing all global energy with wind, water, and solar power, Part II: reliability, system and transmission costs, and policies**. *Energy Pol* 2011, **39**: 1170–1190.
2. Jacobson MZ, Delucchi MA: **Providing all global energy with wind, water, and solar power, Part I: technologies, energy resources, quantities and areas of infrastructure, and materials**. *Energy Pol* 2011, **39**:1154–1169.
3. Ahualli S, Jiménez ML, Fernández MM, Iglesias G, Brogioli D, Delgado ÁV: **Polyelectrolyte-coated carbons used in the generation of blue energy from salinity differences**. *Phys Chem Chem Phys* 2014, **16**:25241–25246.
4. Barton JP, Infield DG: **Energy storage and its use with intermittent renewable energy**. *IEEE Trans Energy Convers* 2004, **19**:441–448.
5. Brogioli D: **Extracting renewable energy from a salinity difference using a capacitor**. *Phys Rev Lett* 2009, **103**.
6. Brogioli D, La Mantia F: **Heat recovery in energy production from low temperature heat sources**. *AIChE J* 2019, **65**: 980–991.

7. Yang ZG, Zhang JL, Kintner-Meyer MCW, Lu XC, Choi DW, Lemmon JP, Liu J: **Electrochemical energy storage for green grid**. *Chem Rev* 2011, **111**:3577–3613.

8. Higashi S, Lee SW, Lee JS, Takechi K, Cui Y: **Avoiding short circuits from zinc metal dendrites in anode by backside-plating configuration**. *Nat Commun* 2016, **7**:6.

9. Gerstandt K, Peinemann KV, Skilhagen SE, Thorsen T, Holt T: **Membrane processes in energy supply for an osmotic power plant**. *Desalination* 2008, **224**:64–70.

10. Kundu D, Adams BD, Duffort V, Vajargah SH, Nazar LF: **A high-capacity and long-life aqueous rechargeable zinc battery using a metal oxide intercalation cathode**. *Nat Energy* 2016, **1**:8.

11. Senguttuvan P, Han S-D, Kim S, Lipson AL, Tepavcevic S, Fister TT, Bloom ID, Burrell AK, Johnson CS: **A high power rechargeable nonaqueous multivalent Zn/V2O5 battery**. *Adv Energy Mater* 2016, **6**:1600826.

12. Trocoli R, La Mantia F: **An aqueous zinc-ion battery based on copper hexacyanoferrate**. *ChemSusChem* 2015, **8**:481–485.

13. Gonzalez MA, Trocoli R, Pavlovic I, Barriga C, La Mantia F: **Layered double hydroxides as a suitable substrate to improve the efficiency of Zn anode in neutral pH Zn-ion batteries**. *Electrochem Commun* 2016, **68**:1–4.

14. Sun KEK, Hoang TKA, Doan TNL, Yu Y, Zhu X, Tian Y, Chen P: **Suppression of dendrite formation and corrosion on zinc anode of secondary aqueous batteries**. *ACS Appl Mater Interfaces* 2017, **9**:9681–9687.

15. Hashemi AB, Kasiri G, La Mantia F: **The effect of polyethyleneimine as an electrolyte additive on zinc electrodeposition mechanism in aqueous zinc-ion batteries**. *Electrochim Acta* 2017, **258**:703–708.

16. * Liu Z, Bertram P, Endres F: **Bio-degradable zinc-ion battery based on a prussian blue analogue cathode and a bio-ionic liquid-based electrolyte**. *J Solid State Electrochem* 2017, **21**: 2021–2027.

First full zinc-ion cell operating in water/bio-ionic liquid.

17. Hashemi AB, La Mantia F: **Cell design for electrochemical characterizations of metal -ion batteries in organic and aqueous electrolyte**. *Anal Chem* 2016, **88**:7916–7920.

18. Zhang L, Chen L, Zhou X, Liu Z: **Towards high-voltage aqueous metal-ion batteries beyond 1.5 V: the zinc/zinc hexacyanoferrate system**. *Adv Energy Mater* 2015, **5**:1400930.

19. Beck F, Rüetschi P: **Rechargeable batteries with aqueous electrolytes**. *Electrochim Acta* 2000, **45**:2467–2482.

20. Gupta T, Kim A, Phadke S, Biswas S, Luong T, Hertzberg BJ, Chamoun M, Evans-Lutterodt K, Steingart DA: **Improving the cycle life of a high-rate, high-potential aqueous dual ion battery using hyper-dendritic zinc and copper hexacyanoferrate**. *J Power Sources* 2016, **305**:22–29.

21. Pourbaix M: *Atlas of electrochemical equilibria in aqueous solutions.* National Association of Corrosion Engineers; 1974.

22. Dushina A, Stojadinovic J, La Mantia F: **Effect of the mass transport limitations on the stability window of electrolytes for metal-ion batteries**. *Electrochim Acta* 2015, **167**:262–267.

23. Hashemi AB, Kasiri G, Glenneberg J, Langer F, Kun R, La Mantia F: **Electrochemical and morphological characterization of Zn-Al-Cu layered double hydroxides as a negative electrode in aqueous zinc-ion batteries**. *ChemElectroChem* 2018, **5**:2073–2079.

24. Shen Y, Kordesch K: **The mechanism of capacity fade of rechargeable alkaline manganese dioxide zinc cells**. *J Power Sources* 2000, **87**:162–166.

25. Lee J, Ju JB, Cho WI, Cho BW, Oh SH: **Todorokite-type MnO2 as a zinc-ion intercalating material**. *Electrochim Acta* 2013, **112**:138–143.

26. Lee B, Lee HR, Kim H, Chung KY, Cho BW, Oh SH: **Elucidating the intercalation mechanism of zinc ions into α-MnO2 for rechargeable zinc batteries**. *Chem Commun* 2015, **51**: 9265–9268.

27. Eckert M, Peters W, Drillet JF: **Fast microwave-assisted hydrothermal synthesis of pure layered delta-MnO2 for multivalent ion intercalation**. *Materials* 2018, **11**:18.

28. Sambandam B, Soundharrajan V, Kim S, Alfaruqi MH, Jo J, Kim S, Mathew V, Sun YK, Kim J: **Aqueous rechargeable Zn-ion batteries: an imperishable and high-energy Zn2V2O7 nanowire cathode through intercalation regulation**. *J Mater Chem A* 2018, **6**:3850–3856.

29. Tang B, Fang G, Zhou J, Wang L, Lei Y, Wang C, Lin T, Tang Y, Liang S: **Potassium vanadates with stable structure and fast ion diffusion channel as cathode for rechargeable aqueous zinc-ion batteries**. *Nanomater Energy* 2018, **51**:579–587.

30. Xia C, Guo J, Lei Y, Liang H, Zhao C, Alshareef HN: **Rechargeable aqueous zinc-ion battery based on porous framework zinc pyrovanadate intercalation cathode**. *Adv Mater* 2018, **30**:1705580.

31. Liu Z, Pulletikurthi G, Endres F: **A prussian blue/zinc secondary battery with a bio-ionic liquid-water mixture as electrolyte**. *ACS Appl Mater Interfaces* 2016, **8**:12158–12164.

32. Zhang LY, Chen L, Zhou XF, Liu ZP: **Morphology-dependent electrochemical performance of zinc hexacyanoferrate cathode for zinc-ion battery**. *Sci Rep* 2015, **5**:11.

33. * Kasiri G, Glenneberg J, Bani Hashemi A, Kun R, La Mantia F: **Mixed copper-zinc hexacyanoferrates as cathode materials for aqueous zinc-ion batteries**. *Energy Storage Materials* 2019, **19**:360–369.

Detailed study on the electrochemical performance and on the morphological changes of mixed CuZnHCF with higher energy density and cycle life.

34. Hurlbutt K, Wheeler S, Capone I, Pasta M: **Prussian blue analogs as battery materials**. *Joule* 2018, **2**:1950–1960.

35. Erinmwingbovo C, Palagonia MS, Brogioli D, La Mantia F: **Intercalation into a Prussian blue derivative from solutions containing two species of cations**. *ChemPhysChem* 2017, **18**: 917–925.

36. Itaya K, Uchida I, Neff VD: **Electrochemistry of polynuclear transition metal cyanides: prussian blue and its analogues**. *Accounts Chem Res* 1986, **19**:162–168.

37. Lu Y, Wang L, Cheng J, Goodenough JB: **Prussian blue: a new framework of electrode materials for sodium batteries**. *Chem Commun* 2012, **48**:6544–6546.

38. Moritomo Y, Takachi M, Kurihara Y, Matsuda T: **Thin film electrodes of prussian blue analogues with rapid Li^{+} intercalation**. *APEX* 2012, **5**, 041801.

39. Chapman KW, Chupas PJ, Maxey ER, Richardson JW: **Direct observation of adsorbed H-2-framework interactions in the Prussian blue analogue Mn-3(II) Co-III(CN)(6) (2): the relative importance of accessible coordination sites and van der Waals interactions**. *Chem Commun* 2006:4013–4015.

40. Itaya K, Shoji N, Uchida I: **Catalysis OF the reduction OF molecular-oxygen to water at Prussian blue modified electrodes**. *J Am Chem Soc* 1984, **106**:3423–3429.

41. Wessells CD, Peddada SV, McDowell MT, Huggins RA, Cui Y: **The effect of insertion species on nanostructured open framework hexacyanoferrate battery electrodes**. *J Electrochem Soc* 2012, **159**:A98–A103.

42. Liu S, Pan GL, Li GR, Gao XP: **Copper hexacyanoferrate nanoparticles as cathode material for aqueous Al-ion batteries**. *J Mater Chem A* 2015, **3**:959–962.

43. Itaya K, Uchida I, Neff VD: **Electrochemistry OF polynuclear transition-metal cyanides - Prussian blue and its analogs**. *Accounts Chem Res* 1986, **19**:162–168.

44. Jayalakshmi M, Scholz F: **Performance characteristics of zinc hexacyanoferrate/Prussian blue and copper hexacyanoferrate/Prussian blue solid state secondary cells**. *J Power Sources* 2000, **91**:217–223.

45. Jayalakshmi M, Scholz F: **Charge-discharge characteristics of a solid-state Prussian blue secondary cell**. *J Power Sources* 2000, **87**:212–217.

46. Matsuda T, Moritomo Y: **Two-electron reaction without structural phase transition in nanoporous cathode material**. *J Nanotechnol* 2012, **2012**:8.

47. Ojwang DO, Grins J, Wardecki D, Valvo M, Renman V, Häggström L, Ericsson T, Gustafsson T, Mahmoud A, Hermann RP, Svensson G: **Structure characterization and properties of K-containing copper hexacyanoferrate**. *Inorg Chem* 2016, **55**:5924–5934.

48. Bauer A, Song J, Vail S, Pan W, Barker J, Lu Y: **The scale-up and commercialization of nonaqueous Na-ion battery technologies**. *Adv Energy Mater* 2018, **8**:1702869.

49. Soto MB, Scholz F: **The thermodynamics of the insertion electrochemistry of solid metal hexacyanometallates**. *J Electroanal Chem* 2002, **521**:183–189.

50. Scholz F, Dostal A: **The formal potentials of solid metal hexacyanometalates**. *Angew Chem Int Ed Engl* 1996, **34**: 2685–2687.

51. Zampardi G, Sokolov SV, Batchelor-McAuley C, Compton RG: **Potassium (De-)insertion processes in prussian blue particles: ensemble versus single nanoparticle behaviour**. *Chem Eur J* 2017, **23**:14338–14344.

52. Wang LP, Wang PF, Wang TS, Yin YX, Guo YG, Wang CR: **Prussian blue nanocubes as cathode materials for aqueous Na-Zn hybrid batteries**. *J Power Sources* 2017, **355**:18–22.

53. Zhang LY, Chen L, Zhou XF, Liu ZP: **Towards high-voltage aqueous metal-ion batteries beyond 1.5 V: the zinc/zinc hexacyanoferrate system**. *Adv Energy Mater* 2015, **5**:5.

54. Ni G, Han B, Li QY, Ji Z, Huang B, Zhou CG: **Instability of zinc hexacyanoferrate electrode in an aqueous environment: redox-induced phase transition, compound dissolution, and inhibition**. *ChemElectroChem* 2016, **3**:798–804.

55. Kim D, Lee C, Jeong S: **Iop, A concentrated electrolyte for zinc hexacyanoferrate electrodes in aqueous rechargeable zinc-ion batteries**. In *2017 2nd international conference on innovative engineering materials*. Bristol: Iop Publishing Ltd; 2018.

56. * Chae MS, Hong ST: **Prototype system of rocking-chair Zn-ion battery adopting zinc chevrel phase Anode and rhombohedral zinc hexacyanoferrate cathode**. *Batter Basel* 2019, **5**:13.

First full-cell rocking chair aqueous Zn-ion battery based on a PBA positive electrode.

57. Jia ZJ, Wang BG, Wang Y: **Copper hexacyanoferrate with a well-defined open framework as a positive electrode for aqueous zinc ion batteries**. *Mater Chem Phys* 2015, **149**: 601–606.

58. Kasiri G, Trocoli R, Hashemi AB, La Mantia F: **An electrochemical investigation of the aging of copper hexacyanoferrate during the operation in zinc-ion batteries**. *Electrochim Acta* 2016, **222**:74–83.

59. ** Renman V, Ojwang DO, Valvo M, Gomez CP, Gustafsson T, Svensson G: **Structural-electrochemical relations in the aqueous copper hexacyanoferrate-zinc system examined by synchrotron X-ray diffraction**. *J Power Sources* 2017, **369**: 146–153.

Detailed in-operando study of the crystal structure variation of CuHCF upon the initial Zn (de-)insertion.

60. ** Lim J, Kasiri G, Sahu R, Schweinar K, Hengge K, Raabe D, La Mantia F, Scheu C: **Irreversible structural changes of copper hexacyanoferrate used as cathode in Zn-ion batteries**. *Chem Eur J* 2019, https://doi.org/10.1002/chem.201905384.

Detailed study on the morphological changes of the particles of CuHCF upon long term cycling and on their possible composition.

61. * Trocoli R, Kasiri G, La Mantia F: **Phase transformation of copper hexacyanoferrate (KCuFe(CN)(6)) during zinc insertion: effect of co-ion intercalation**. *J Power Sources* 2018, **400**: 167–171.

Insight into the phase transitions occurring during the CuHCF cycling.