



# Improving the cycle life of a high-rate, high-potential aqueous dual-ion battery using hyper-dendritic zinc and copper hexacyanoferrate



Tanya Gupta<sup>a</sup>, Andrew Kim<sup>a</sup>, Satyajit Phadke<sup>a</sup>, Shaurjo Biswas<sup>a</sup>, Thao Luong<sup>b</sup>, Benjamin J. Hertzberg<sup>a</sup>, Mylad Chamoun<sup>c</sup>, Kenneth Evans-Lutterodt<sup>c</sup>, Daniel A. Steingart<sup>a,\*</sup>

<sup>a</sup> Department of Mechanical and Aerospace Engineering The Andlinger Center for Energy and The Environment, Princeton University, NJ 08544, USA

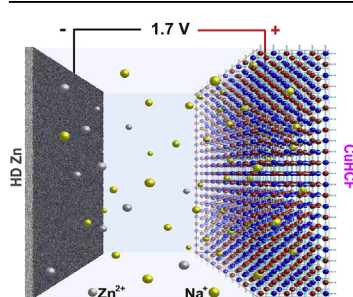
<sup>b</sup> University of California, Los Angeles, CA 90095, USA

<sup>c</sup> Brookhaven National Laboratory, Upton, NY 11973, USA

## HIGHLIGHTS

- Improved performance of a Prussian Blue Analogue vs. Zn battery.
- 90% capacity retention after 300 cycles is achieved.
- Preferential intercalation of Na<sup>+</sup> over Zn<sup>2+</sup> is exploited.
- Use of Hyper-Dendritic Zinc to improve kinetics.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 21 September 2015

Received in revised form

1 November 2015

Accepted 17 November 2015

Available online 29 November 2015

### Keywords:

Prussian blue analogue

Hyper-dendritic zinc

*In situ* EDXRD

Aqueous dual ion battery

High capacity retention

Long battery cycle life

## ABSTRACT

Prussian Blue Analogue (PBA)-Zn aqueous batteries are attractive because of the high potential of PBA against Zn (~1.7 V), relative safety of the system, and high rate capability. But, despite the long cycle life of PBA half-cells, full PBA-Zn battery systems studied thus far have typically reported only up to 100 cycles and suffer significant capacity fade beyond that. In this work we demonstrate that the loss in capacity retention and cycle life is a combined effect of Zn<sup>2+</sup> ion poisoning at the PBA cathode, as well as dendrite formation in the zinc anode. We address both these issues via the use of a dual ion (Na<sup>+</sup> as the primary charge carrier) electrolyte and hyper-dendritic Zinc (HD Zn) as the anode. The copper hexacyanoferrate (CuHCF) vs. HD Zn system with Na<sup>+</sup> ion electrolyte demonstrated herein exhibits 90% (83%) capacity retention after 300 (500) cycles at a 5C rate and a 3% reduction in usable capacity from 1C to 5C. Detailed characterization is done using *in situ* synchrotron energy-dispersive XRD (EDXRD), conventional XRD, XPS, SEM, TEM, and electrochemical techniques.

© 2015 Elsevier B.V. All rights reserved.

## 1. Background and motivation

Prussian blue (PB) analogue electrodes have gained considerable attention due to their low cost, long cycle life and exceptional rate capability. The open cage-like structure allows for rapid intercalation/deintercalation of various cations without significant

\* Corresponding author. Room D428, Engineering Quadrangle, Olden St., Princeton, NJ 08544-5263, USA.

E-mail address: [steingart@princeton.edu](mailto:steingart@princeton.edu) (D.A. Steingart).

change to the crystal structure [1–5]. The long cycle life, fast kinetics, and relative safety makes them suitable candidates for grid scale energy storage as well as wearable, flexible electronics. Several attempts have been made to build a complete battery using these electrodes. Wessels et al. [6] demonstrated Ni–Cu PB analogues for both electrodes and tuned the potential between the working and counter electrodes by changing the Ni:Cu ratio, although the maximum potential difference achieved was relatively low, of the order 0.4 V. The CuI group [7] used activated carbon/polypyrrole hybrid electrodes vs. PBA to achieve an OCV of 1.2 V, albeit with the downside of specific energy of 5 Wh kg<sup>-1</sup> at a rate of 20 C.

A recent development in Prussian blue analogues (PBAs) is the use of Zn as counter electrode. Zinc, like PBA, is low cost and relatively benign. More importantly, PBAs have a high potential (~1.7 V) vs. Zn in aqueous electrolyte. In addition, this couple exhibits high energy and fast kinetics making it suitable for high power applications for grid scale frequency regulation and peak shaving applications, markets where California has demanded the installation of 1.3 GW of power handling between 10 and 30 min duration in the next decade. Zhang et al. [8] demonstrated reversible cycling of Zn<sup>2+</sup> ions in zinc hexacyanoferrate (ZnHcf) cathodes and Zn anodes. However, cycling Zn<sup>2+</sup> in ZnHcf exhibits a low capacity retention of 81% after 100 cycles [8]. Cycling of Zn<sup>2+</sup> in copper hexacyanoferrate (CuHcf) has also been investigated [9,10]. It was demonstrated that Zn<sup>2+</sup> ions in CuHcf cathodes show 96.3% capacity retention for 100 cycles at pH 6 [10]. But, as shown later, when these experiments were repeated in our lab, we observed a drastic degradation in capacity immediately after an equivalent of 100 cycles for an identical battery system. The fade rate suggests that repeated removal and insertion of Zn<sup>2+</sup> ions irreversibly damages the crystal structure of ZnHcf or CuHcf eventually. Moreover, the maximum specific capacity of CuHcf cells has been found to be 60 mAh g<sup>-1</sup> [11], regardless of the valency of the intercalating ion. This may seem counterintuitive, as one may expect the capacity of the battery to scale with increasing ionic charge. However, for mass loadings typical of CuHcf electrodes reported thus far, the concentration of ions in the electrolyte far exceed the available sites in the PBA crystal structure. To maintain charge balance, the number of sites occupied by the intercalating species will depend on the number of Fe<sup>2+</sup> available for oxidation in the PBA crystal, which is the primary mechanism of storage [12,13]. This implies that it is the number of Fe<sup>2+</sup> in the crystal structure that limits the cell capacity. Hence, the capacity of a CuHcf battery is insensitive to the ionic valency of the intercalating species, provided that its concentration in the electrolyte exceeds the moles of active material.

Thus, using Zn<sup>2+</sup> as the intercalating species has no inherent advantage, in terms of specific capacity, over monovalent ions. In fact, a rather short cycle life and sharp capacity fade is seen in systems with Zn<sup>2+</sup> ions and Zn anode [8,10]. We believe this behavior can be attributed to two major factors: *i*) cyclability of Zn<sup>2+</sup> ions in PBA is not as reversible as other highly studied ions like Na<sup>+</sup>, K<sup>+</sup>, as it has been shown in the past [11,14] that chemical stability of PBAs is highly sensitive to the intercalating ion; and *ii*) passivation of Zn and formation of Zn dendrites leads to slow degradation in capacity.

In this work, we demonstrate a battery framework that systematically addresses both these factors and exhibits exceptional performance when compared to previously known PBA–Zn systems. CuHcf is preferentially used as the cathode in our experiments over ZnHcf, since it has been extensively studied and is known to be stable over extended cycle times [13]. Additionally, hyper-dendritic zinc (HD Zn) is used as the anode to replace the conventional sheet Zn, and a 1 M Na<sub>2</sub>SO<sub>4</sub>/0.01 M H<sub>2</sub>SO<sub>4</sub> solution

acts as the aqueous electrolyte. HD Zn is shown here to improve the performance of the Zn electrode, which otherwise forms dendrites [15–19] and limits the cycle life of the system. Detailed characterization of the active materials of the battery system is done using *in situ* synchrotron energy-dispersive X-ray diffraction (EDXRD), conventional XRD, SEM, TEM, XPS and various electrochemical techniques. Effect of aging on the extent of zinc poisoning is included in the [Supplemental Information](#).

## 2. Experimental methods

### 2.1. Copper hexacyanoferrate (CuHcf) electrode

The synthesis of CuHcf and subsequent fabrication of the slurry electrode is done by the same process as described elsewhere [13]. Briefly, 100 ml of 0.1 M copper nitrate and 100 ml of 0.05 M potassium hexacyanoferrate (III) were simultaneously added drop wise to 50 ml of deionized water, while it was continuously stirred. Immediate precipitation of CuHcf particles is observed. The resulting suspension is sonicated for 20 min and allowed to rest overnight. It is then washed with water to remove residual reactants and filtered to obtain a greenish-yellow powder of CuHcf. Detailed characterization of CuHcf particles has been done previously [13]. Slurry electrodes are used, as they enable higher mass loadings. The mass loading of the active material was ~4 mg cm<sup>-2</sup>. Active material, carbon black, graphite, and polystyrene binder are mixed in a 1.5:1:1:0.5 weight ratio to form a slurry. It should be noted that a trace amount (~5 μl) of the surfactant Triton × 100 is added to 4 g of the slurry to wet the substrate (carbon cloth) effectively. The SEM images (Fig. 1d) of the slurry on carbon cloth show the wetting of the substrate, which is found to be better upon addition of the surfactant.

### 2.2. Hyper dendritic zinc (HD Zn) electrode

For the anode, HD zinc is electroplated on a sheet of Zn metal (McMaster-Carr) in a 8.9 M KOH/0.61 M ZnO electrolyte at –2.0 V vs. Hg/HgO [20]. Nickel is used as a counter electrode. The HD zinc electrode is washed in water and then in 0.01 M H<sub>2</sub>SO<sub>4</sub> to reduce the zinc oxide layer formed, and to neutralize any residual KOH from the electrolyte. Fig. 8a shows the morphology of the HD Zn used in this study.

### 2.3. Electrochemical testing

Constant current charge and discharge is performed for two-electrode setups at different rates based on the mass of active material (CuHcf) and a theoretical capacity of 60 mAh g<sup>-1</sup>. A 1 min rest time between charge and discharge is used to allow equilibration of the electrodes. A three-electrode flooded cell setup is used for cyclic voltammetry at 1 mV s<sup>-1</sup> with Ag/AgCl as the reference electrode and zinc as counter. All results shown are using HD Zn unless mentioned otherwise. All experiments were done at 298 K.

### 2.4. *In situ* X-ray diffraction

Synchrotron X-Ray microdiffraction was carried out by the same method as described by Gallaway et al. [21] at the Brookhaven National Laboratory. We used the X13B beam line where X-rays of wavelength 0.65 Å were focused onto the working electrode of the cell to a spot size of 2 μm × 2 μm. Cell was constructed with a X-ray transparent polymer and thin walls (~1 mm) to minimize the noise to signal ratio. X-ray spectra were collected after every 1 min.

Download English Version:

<https://daneshyari.com/en/article/1285530>

Download Persian Version:

<https://daneshyari.com/article/1285530>

[Daneshyari.com](https://daneshyari.com)