Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Sample dependent performance of aqueous copper hexacyanoferrate/zinc batteries

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Cycle life comparison for selected cells

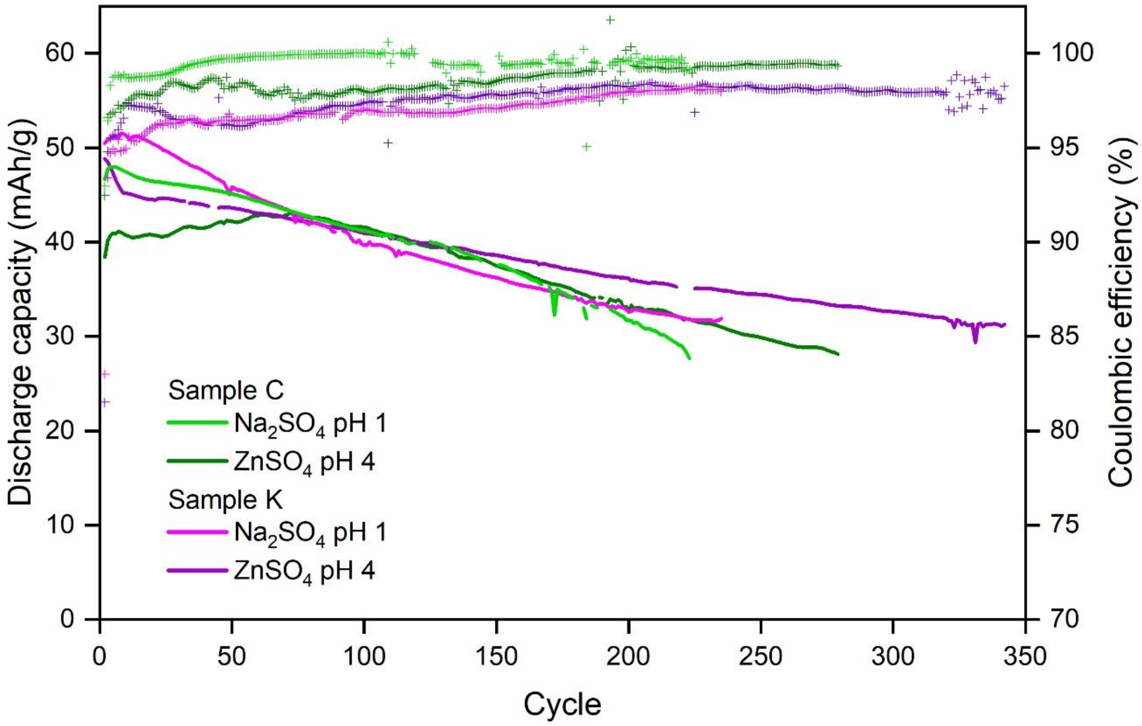

Figure S1: Discharge capacity and Coulombic efficiency as a function of cycle for samples C and K as cathode material in CuHCF/Zn cells with Na_2SO_4 electrolyte at pH 1 and $ZnSO_4$ electrolyte at pH 4. Cells are cycled in the voltage range 1.4-2.0 V with a current rate of 50 mA/g.

Addition of ZnO to CuHCF/Zn cells with Na-based electrolyte

CuHCF/Zn cells with Na_2SO_4 electrolyte must contain enough Zn^{2+} to enable full reduction. Figure S2 shows two CuHCF/Zn cells with Na_2SO_4 electrolyte with and without added ZnO for comparison. There is no difference in performance whether ZnO is added or not.

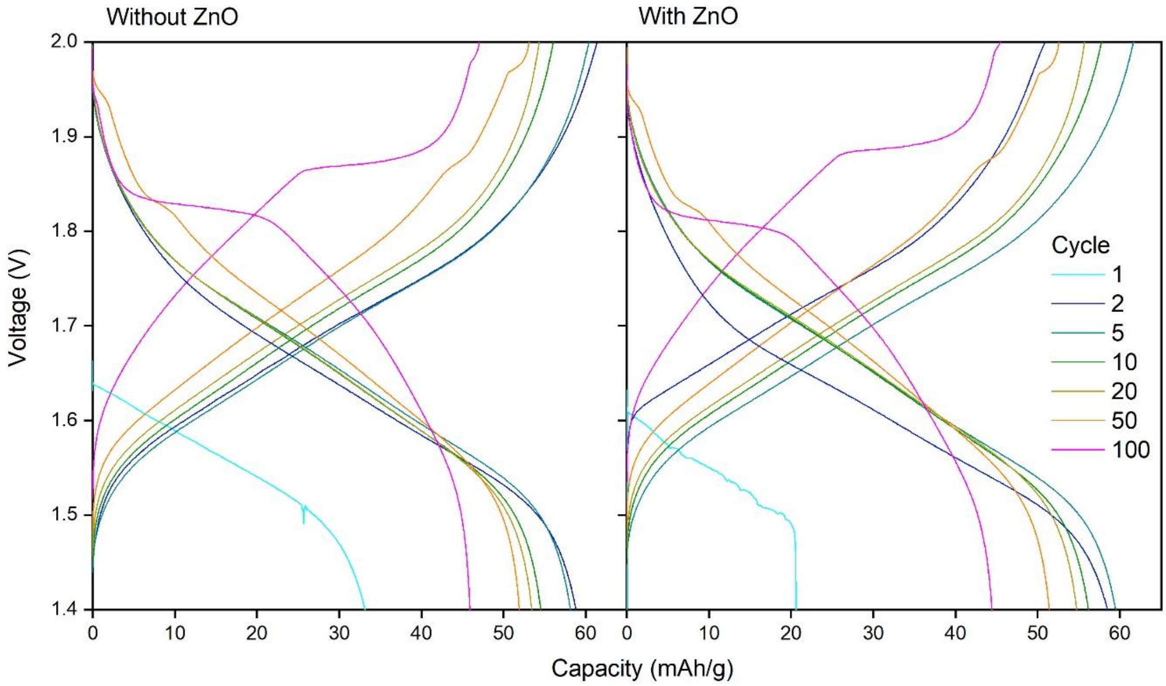

Figure S2: CuHCF/Zn cells with Na_2SO_4 electrolyte at pH 1, with at without added ZnO. CuHCF is sample G.

Proton intercalation

At very low pH there are a large number of protons available, which could potentially intercalate in the CuHCF framework. It has previously been reported that proton insertion does not account for the electrochemical features observed for PBA in acidic Na^+/Zn^{2+} electrolyte: Wang *et al.* compared CVs of PBA in 1 M M^{2+} electrolyte at pH 2 and in nitric acid electrolyte at pH 2, showing that H^+ insertion does not account for the electrochemical features in 1 M M^{2+} electrolyte.[1] Gupta *et al.* compared CVs of PBA in acidified $ZnSO_4$ electrolyte and acidified Na_2SO_4 electrolyte with H_2SO_4 electrolyte, confirming that H^+ is not the intercalating species.[2]

Sample K long term cycling

Long term cycling of CuHCF/Zn cell with sample K cathode reveals that the plateau at 1.85 V develops after 400 cycles.

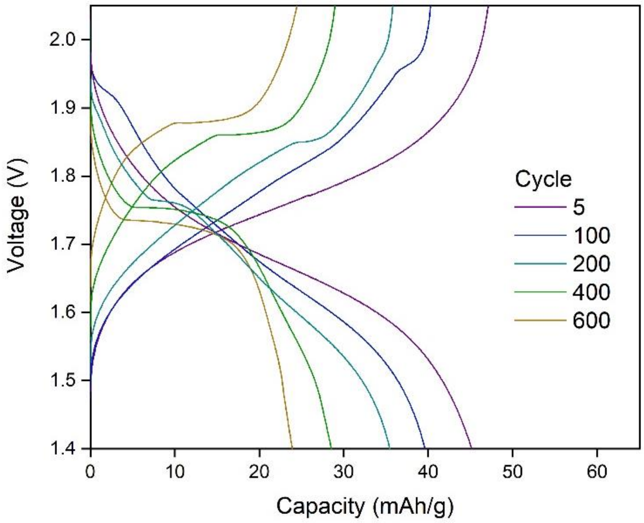

Figure S3: Capacity/voltage plots for CuHCF/Zn cell with sample K cathode in $ZnSO_4$ electrolyte at pH 4. The cell is cycled in the voltage range 1.4-2.0 V with a current rate of 50 mA/g.

Cap/vol before and after 5 months break

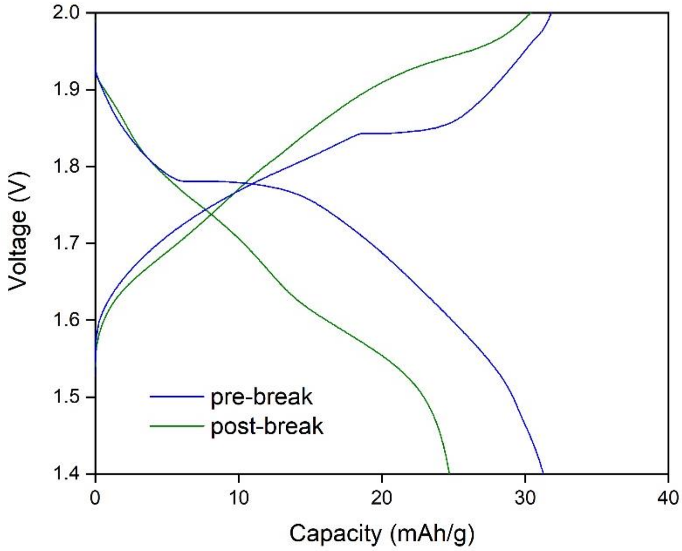

Figure S4: Capacity/voltage plots for CuHCF/Zn cell with sample K cathode in $ZnSO_4$ electrolyte at pH 4 immediately before and after resting the cell for five months. The cells is cycled in the voltage range 1.4-2.0 V with a current rate of 50 mA/g.

Difference in voltage profile for sodium and zinc-containing electrolytes

CuHCF/Zn cells cycled in voltage range 0.8-1.9 V. The low voltage plateau which is observed for CuHCF/Zn cells with $ZnSO_4$ electrolyte is less pronounced in Na_2SO_4 electrolyte.

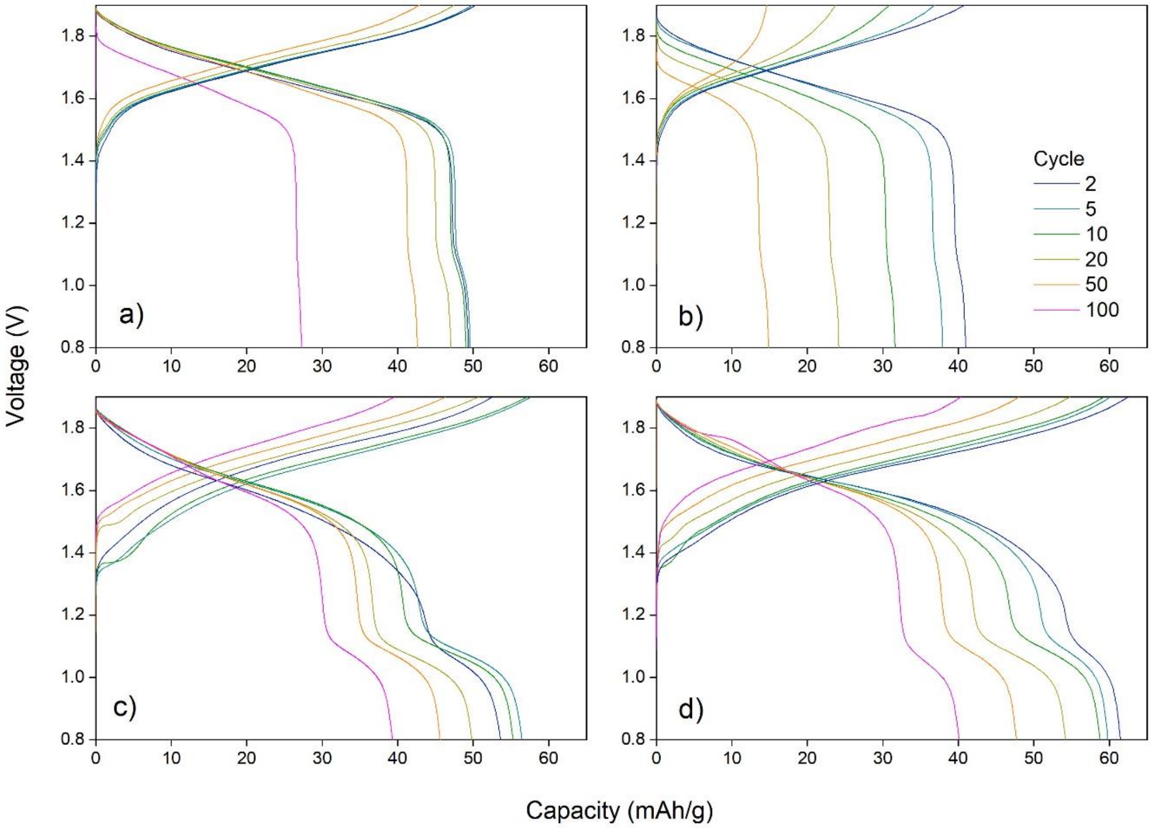

Figure S5: Capacity/voltage plots for CuHCF/Zn cells, sample C. a) 1 M Na_2SO_4 + 0.05 M H_2SO_4, b) 1M Na_2SO_4, c) 1 M $ZnSO_4$ + 0.05 M H_2SO_4 and d) 1M $ZnSO_4$

Zn^{2+} concentration in Na_2SO_4 electrolyte

The volume of electrolyte in the coin cells was approximately 0.14 mL. The volume of the electrolyte was calculated based on the difference between the weight of cell parts before assembly and the mass of the coin cell. The Zn^{2+} concentration in the electrolyte is highest when the cell is discharged.

Based on a volume of 0.14 mL electrolyte, and a capacity of 0.4 mAh which is representative for the cells in the current study, the maximum concentration of Zn^{2+} ions in the electrolyte is calculated as follows:

$$\frac{0.4\ mAh}{26{,}801\ mAh/mol} = 1.49 \cdot 10^{-5} mol$$

$$\frac{1.49 \cdot 10^{-5} mol}{0.00014\ L} = 0.1\ M\ Zn^{2+}$$

Low vacancy cathode

Initial tests have been carried out with low vacancy MnHCF ($K_{1.86}Mn[Fe(CN)_6]_{0.97}$, sample L in our previous work) as cathode for aqueous Zn-ion batteries with $ZnSO_4$ electrolyte. The cycle life is rather poor, see figure S6. During the initial cycles, the Coulombic efficiency is very low, resulting in significant capacity loss. After the first five cycles, the Coulombic efficiency has increased to 75 %, and after 15 cycles it reaches 97 %. Although the capacity decreases rapidly, the results for the MnHCF/Zn cell gives an indication that low vacancy PBA are viable for aqueous Zn-ion batteries. Despite reports that larger cations move via vacancies, low vacancy PBA seem to be able to reversibly intercalate Zn-ions in aqueous electrolyte.

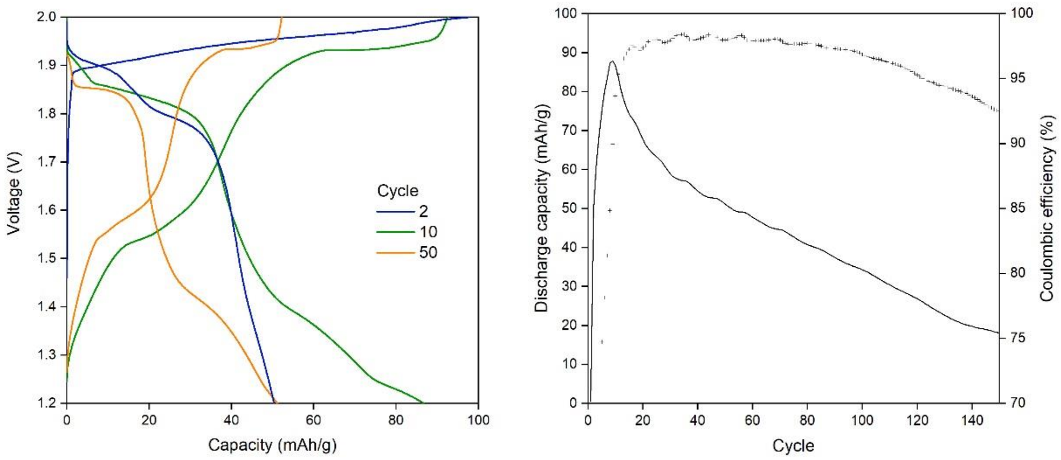

Figure S6: Low vacancy MnHCF as cathode for MnHCF/Zn cell with 1 M $ZnSO_4$ electrolyte at pH 2. The cell is cycled in the voltage range 1.2-2.0 V with a current rate of 50 mA/g.

References

1 R. Y. Wang, C. D. Wessells, R. A. Huggins and Y. Cui, *Nano Lett.*, 2013, **13**, 5748–5752.

2 T. Gupta, A. Kim, S. Phadke, S. Biswas, T. Luong, B. J. Hertzberg, M. Chamoun, K. Evans-Lutterodt and D. A. Steingart, *J. Power Sources*, 2016, **305**, 22–29.