A Symmetric Aqueous Electrolyte Prussian Blue Analogue Battery For Stationary Storage Applications

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New types of energy storage are needed in conjunction with the deployment of solar, wind, and other volatile renewable energy sources and their integration with the electrical grid. No existing energy storage technology can provide the power, cycle life, and energy efficiency needed to respond to the costly short-term transients that arise from renewables and other aspects of grid operation[1].

Recently, we developed a family of open framework nanoparticle materials with the Prussian Blue crystal structure. This crystal structure is composed of a face-centered cubic framework of transition metal cations that are octahedrally coordinated to hexacyanometalate groups. Large interstitial "A Sites" within the structure can accommodate zeolitic water and hydrated alkali ions. This results in a general chemical formula of $A_xPR(CN)_6 \bullet nH_2O$, where A is an alkali cation such as K^+ or Na^+, P is a transition metal cation such as Cu^{2+}, Ni^{2+}, Mn^{2+} or Fe^{3+}, and $R(CN)_6$ is a hexacyanometalate anion such as $[Fe(CN)_6]^{3-}$, $[Mn(CN)_6]^{3-}$, or $[Cr(CN)_6]^{3-}$. The Prussian Blue framework structure has wide channels between the A sites, allowing for rapid insertion and removal of Na^+, K^+, and other ions from aqueous solutions with little lattice strain. The result is an extremely stable electrode: over 40,000 deep discharge cycles were demonstrated in the case of copper hexacyanoferrate (CuHCFe)[2]. In particular, the reaction potential of 0.95 V vs. SHE, room temperature synthesis, low cost and long cycle life make CuHCFe the perfect cathode candidate in an aqueous electrolyte battery for grid-scale storage applications.

The CuHCFe cathode must be paired with an anode that has comparable cycle life and kinetics to avoid a substantial loss in performance for the full battery. The activated charcoal used in commercial ultracapacitors has these properties, and we recently showed that it could be successfully combined with the CuHCFe cathode in an asymmetric cell[3]. However, the low capacity of capacitive electrodes such as activated charcoal severely limited the specific energy of this cell. Prussian Blue analogues that use hexacyanometallates of Mn, Cr, Co, and Ru, among others, have long been studied for their magnetic and structural properties; however, their electrochemical properties have received very little attention.

Here, we demonstrate a new type of safe, fast, inexpensive, long-cycle life aqueous electrolyte battery, which relies on the insertion of sodium ions into the previously reported copper hexacyanoferrate cathode and a newly developed manganese(II) hexacyanomanganate anode, each of which have the same open framework crystal structure (Figure 1). This high rate, high efficiency cell has a 96.7% round trip energy efficiency when cycled at a 5C rate, and a 84.2% energy efficiency at 50C.

There is zero capacity loss after 1000 deep-discharge cycles. Bulk quantities of the electrode materials are produced by a room temperature chemical synthesis from earth-abundant precursors, and the cell operates in a safe and inexpensive aqueous sodium-ion electrolyte.

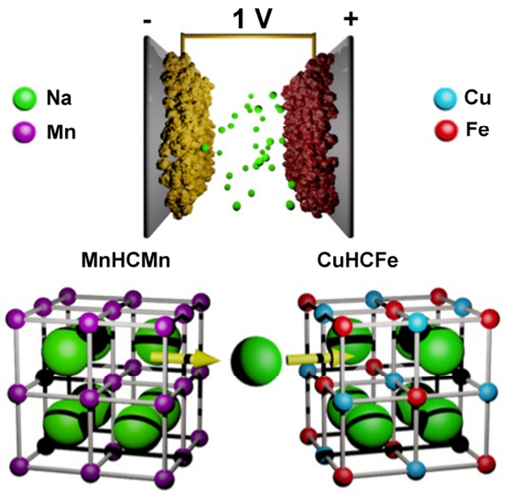

Figure 1. Full cell schematic showing the copper hexacyanoferrate (CuHCFe) cathode and the manganese hexacyanomanganate (MnHCMn) anode, each of which have the same open framework crystal structure.

References:

1. Yang, Z. et al. *Electrochemical Energy Storage for Green Grid*. Chem. Rev. 111, 3577-3613 (2011).
2. C. D. Wessells, R. A. Huggins, Y. Cui, *Copper hexacyanoferrate battery electrodes with long cycle life and high power*. Nat Commun 2, 550 (2011).
3. M. Pasta, C. D. Wessells, R. A. Huggins, Y. Cui, *A high-rate and long cycle life aqueous electrolyte battery for grid-scale energy storage*. Nat Commun 3, 1149 (2012).