

Safe, Inexpensive, Long Life, High Power and Efficiency Batteries For Grid Scale Energy Storage Applications

Investigators

Yi Cui, Associate Professor; Robert Huggins, Professor; Mauro Pasta, Postdoctoral researcher; Hyun Wook Lee, Postdoctoral researcher; Richard Wang, Graduate Researcher, Materials Science and Engineering, Stanford University.

Abstract

New types of energy storage are required in conjunction with the deployment of renewable energy sources and their integration with the electrical grid. A new kind of energy storage technology is needed for short-term grid storage applications, as existing technology struggle to meet the needs of these applications at a reasonable price.

We previously introduced a new family of cathode materials involving the reversible insertion of cations into materials with the Prussian Blue open-framework (OF) crystal structure. We showed that copper hexacyanoferrate (CuHCF) electrodes are particularly promising because of their ultra-long cycle life, high power, high-energy efficiency, and potentially, a very low-cost.

OF structure cathodes are ideally paired with an anode that has comparable cycle life and kinetics to avoid a substantial constraint in the performance of the full battery. In the past year, we have made progress in this area by developing two different classes of anode materials: a novel hybrid activated carbon/polypyrrole anode, which has the high rate capability of an ultracapacitor and the well-defined potential of a battery electrode and a newly developed manganese hexacyanomanganate open-framework anode. By combining these novel anodes with CuHCFe we introduced new types of safe, fast, inexpensive, long-life aqueous electrolyte batteries. These properties make them attractive for grid-related applications.

We have also demonstrated divalent ions insertion in OF materials. Searching for battery materials for divalent ion interaction is an exciting direction to enable potentially low-cost battery for grid-scale storage. We have shown that materials like nickel hexacyanoferrate (NiHCF) and CuHCFe, can reversibly intercalate aqueous alkaline earth divalent ions such as: Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} . Our results represent a step forward and pave the way for future development in divalent intercalation batteries.

Introduction

Renewable energy such as solar and wind will be increasingly used in the future to address the climate change and energy dependence problems. Grid-connected electrical energy storage is important for enabling full utilization of renewable electricity generation from solar and wind energy-harvesting devices connected to grids, largely due to the fluctuations of devices on multiple time scales. Electrochemical energy storage technologies such as batteries and electrochemical capacitors are promising but the cost in terms of \$/kWh is too high.

This project aims at the discovery and development of materials to be used in stationary electrochemical energy storage systems of the magnitudes, with the kinetic characteristics, with low-cost potential, applicable to their application to support wind and solar systems and their integration with the large-scale electrical energy distribution system.

A focus materials system here is the family of Prussian Blue open framework materials. They have characteristic of low-cost, high-rate, long cycle life, working in both aqueous and organic electrolyte. We aim to develop both anodes and cathodes of open framework materials and explore the related electrochemistry towards high performance grid-scale storage.

Background

In the past year, external research progress related to grid-scale electrochemical energy storage includes the following:

Redox flow batteries continue to be an interesting direction for the grid scale storage. The key challenges are how to reduce the cost, the anolyte and catholyte liquid crossing, to improve the ion conducting membrane. One key aspect is related to the energy density of flow batteries. It becomes important for reducing the cost of battery system if high-energy redox flow battery is enabled. So searching for redox couples with high solubility is an exciting direction to go.

Batteries/supercapacitors based on aqueous electrolyte continues to make progress. A notable example is from the company Aquion, which use NaMnOx cathode and capacitive carbon anodes. The energy density and cycle life are improved.

Li-ion batteries continue to be explored for grid-scale storage although the cost is still too high. The possibility of employing LIB previously used on electric vehicles (EV) on the grid has been explored. Models to predict their residual cycle life is an interesting research area.

Compared to the external research developments, the project here shows the potential advantages of low-cost, high power rate and long cycle life.

Results

Aqueous batteries with hybrid activated carbon/polypyrrole anodes

We described a new class of anodes that are compatible with the previously reported open framework CuHCF materials in aqueous electrolytes. These anodes are based on a hybrid electrode that operates by a new fundamental concept: by combining an electrode material (polypyrrole, PPy) that is capable of a faradaic reaction at a fixed potential with a capacitive electrode (activated carbon), the potential of the entire electrode can be controlled. Fundamentally different from traditional capacitive and battery electrodes, our new hybrid electrode has the high rate capability of an ultracapacitor but with the well-defined electrochemical potential of a battery electrode. This hybrid electrode has attractive open circuit potential

(OCP) tunable to -0.2 V versus SHE, a shallow charge/discharge profile and low self-discharge.

We demonstrated that a full cell with this hybrid anode and a CuHCF cathode (Figure 1) has performance that is promising for grid-scale stationary storage applications: high power and energy efficiency, and a lifetime of thousands of cycles.

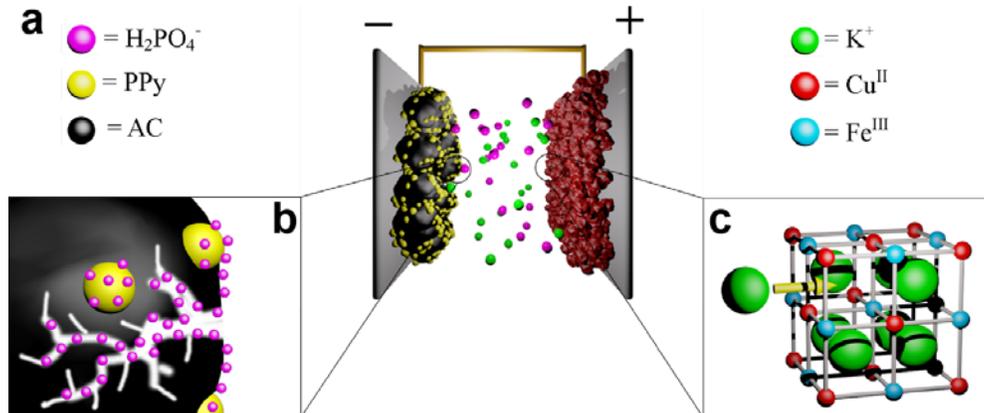


Figure 1. (a) Schematic diagram of full cell device. In the PPy/AC negative electrode (b) the reduced PPy particles fix the open circuit potential close to the lower stability limit of the electrolyte, while the charge is stored in the electrical double layer at the high surface activated carbon. The CuHCF positive electrode (c) has the open framework Prussian Blue crystal structure, in which transition metal ions are linked by a face centered cubic framework of cyanide groups. The framework contains large interstices, known as the "A Sites". This three-dimensional network of A Sites and channels allows for rapid transport of K⁺ through the material without disturbing the framework.

Full cell cycling with potential cutoffs of 0.85 and 1.1 V for the CuHCF cathode resulted in a full cell voltage range of 1.4 to 0.9 V (Fig. 2a,c), and a maximum specific capacity of 54 mAh g⁻¹ CuHCF.

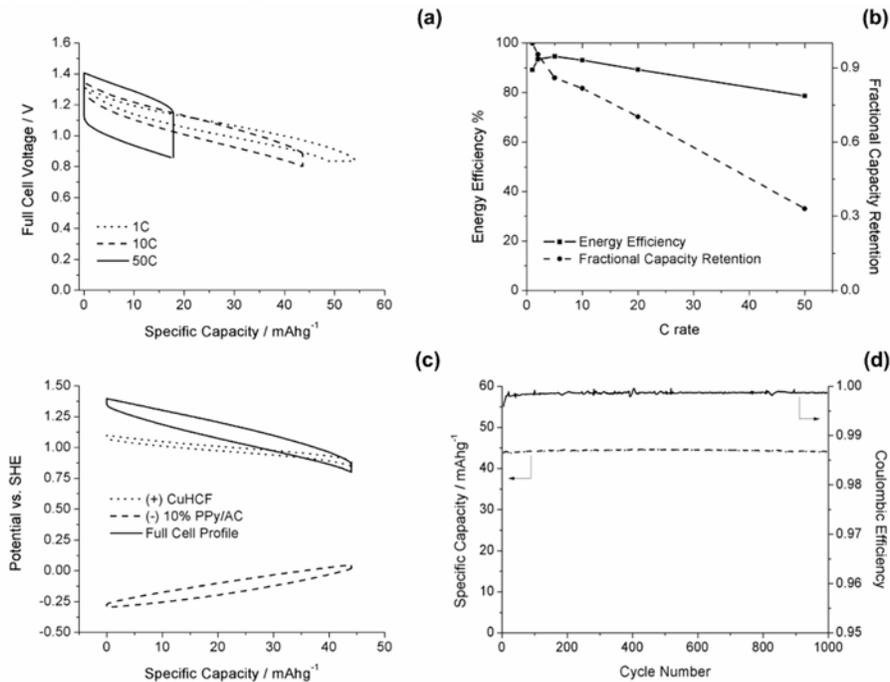


Figure 2. Full cell electrochemical characterization. (a) Full cell potential profiles at different C rates (1C, 10C, 50C) (b) Energy efficiency and fractional capacity retention as a function of the C rate (c)

Potential profiles of copper hexacyanoferrate (CuHCF) positive electrode, 10%Polypyrrole (PPy) /activated carbon (AC) anode negative electrode and full cell profile at 10C, (d) Cycling of the CuHCF-10%PPy/AC cell at a rate of 10C showed no capacity loss after 1000 cycles and a coulombic efficiency of 99.9%.

At a 10C rate, 82% of the maximum specific capacity is retained, with a round trip energy efficiency of 92% (Fig. 2b), and at a rate of 50C, 33% of the maximum specific capacity is observed at an efficiency of 79%. Cycling was highly reversible, with zero capacity loss after 1000 cycles at a 10 C rate, and the coulombic efficiency was 99.9% (Fig. 2d).

The high capacity retention and rate capability of the CuHCF vs. AC/PPy full cells results in high specific power. The average specific power during discharge at a 10C rate during cycling between 1.4 and 0.9 V was 45 W/kg on the basis of the electrode active materials, and a maximum specific power of nearly 100 W/kg was achieved at 20C. The specific energy of the cells reported here was about 5 Wh/kg, lower than conventional lithium ion, lead acid and NiMH batteries. However, as the discharge voltage was limited to 0.9 V, all of the specific energy of the cell can be practically used.

Full open framework batteries

The specific power and energy of the CuHCF vs. AC/PPy cell previously described is limited by the high mass loading of the anode. This motivated us in developing improved anode materials. We reported the use of manganese hexacyanomanganate (MnHCMn) as an anode material that has the same open framework structure but a low reaction potential, around 0 V vs. SHE, and when combined with cathodes such as CuHCFe, yields a useful full cell voltage of about 1 V.

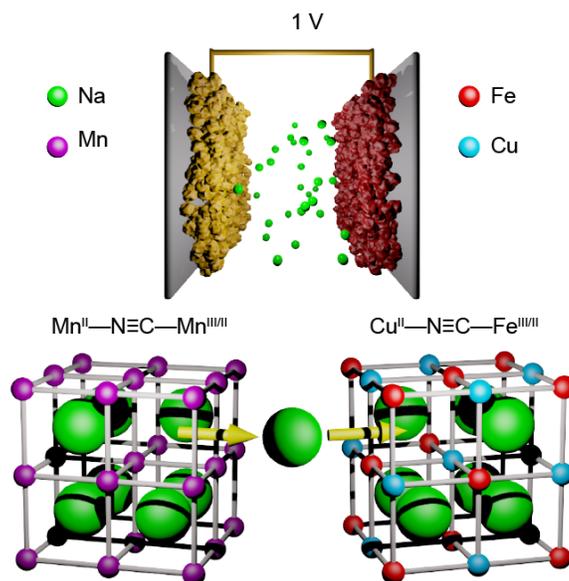


Figure 3. Symmetric open framework cell schematic. This new type of safe, fast, inexpensive, long-cycle life aqueous electrolyte battery relies on the insertion of sodium ions into the copper hexacyanoferrate (CuHCFe) cathode and a newly developed manganese hexacyanomanganate (MnHCMn) anode, each of which have the same open framework crystal structure.

Full batteries containing a CuHCFe cathode, a MnHCMn anode, and excess 10 M NaClO₄ electrolyte were assembled. In such cells, the cathode operates between 1.15 V and 0.85 V vs. SHE, while the anode operates between -0.2 V and 0.2 V (Fig. 4a). This results in a full cell that operates between 1.35 V and 0.65 V, with an average discharge voltage of 0.95 V. Because of the high ionic conductivity of the electrolyte and rapid reaction of the electrodes, very little voltage hysteresis occurs during fast charge and discharge, and little of the nominal voltage of the cell is lost even at a six minute (10C) cycling rate (Fig. 4b). The low voltage hysteresis observed during rapid cycling, along with a high coulombic efficiency of over 99.9%, results in a very high round trip energy efficiency: 95.4% at a 10C rate, and 84.2% even at a 50C rate (Fig. 4c). At a 10C rate, 92.9% of the maximum discharge capacity was retained above 0.65 V, while at a 50C rate, 73.3% was still available.

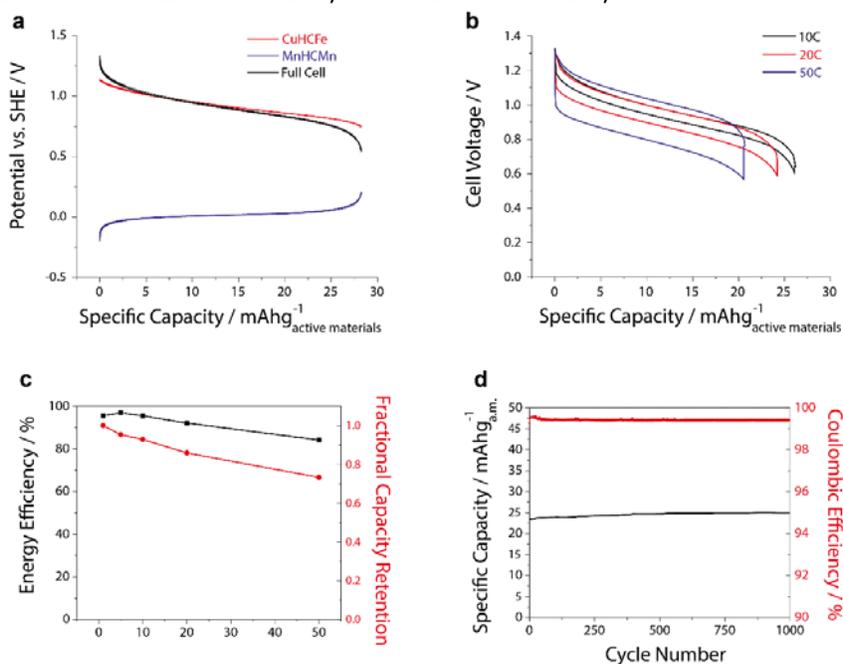


Figure 4 Full cell electrochemical characterization. (a) Potential profiles of the copper hexacyanoferrate (Cu^{II}-N≡C-Fe^{III/II}) positive electrode, the manganese hexacyanomanganate (Mn^{II}-N≡C-Mn^{III/II}) negative electrode and the full cell voltage at a 1C rate. (b) The full cell voltage profiles at different C rates (10C, 20C, 50C). (c) Energy efficiency and fractional capacity retention as a function of C rate. (d) Cycling of the Cu^{II}-N≡C-Fe^{III/II} - Mn^{II}-N≡C-Mn^{III/II} cell at a rate of 10 C showed no capacity loss after 1000 cycles and a coulombic efficiency of 99.8%. (e) The specific energy vs. specific power plot shows intermediate performance between lithium ion batteries and ultracapacitors, ideally positioning this technology for short-term grid-scale energy storage, especially to handle transients.

Extended cycling of full batteries containing a CuHCFe cathode and a MnHCMn anode was also performed. After 1000 cycles at a 10C rate there was no measurable capacity loss (Fig. 4d). The coulombic efficiency during extended cycling was 99.8%.

This novel, symmetric open framework electrode battery delivers a maximum specific energy of 27 Wh/kg at a 1C rate on a basis of the masses of the active materials. Furthermore, this battery has a specific energy of 15 Wh/kg, a specific power of 693 W/kg, and an 84.2% energy efficiency when cycled at a 50C rate.

The electrodes in this battery can be synthesized in bulk and when operated in an appropriate aqueous electrolyte, show extremely long cycle life, fast kinetics, and high efficiency, resulting in a full battery cell that can be an attractive candidate for use in large scale energy storage.

Electrochemical insertion of divalent ions into open framework materials

Recently, divalent magnesium ion insertion has attracted great interest due to magnesium's low cost, elemental abundance, and doubling of electron storage capacity per ion compared to lithium. Studies have demonstrated magnesium insertion in metal chalcogenides, transition metal oxides, and olivines, but finding an electrode material with fast, reversible insertion of divalent magnesium ions remains a major challenge.

Success with monovalent ion insertion has motivated us to explore open framework crystal structure materials for divalent insertion. We demonstrated unprecedented high-rate cycling of nanoscale NiHCF electrodes with Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} ions with long cycle life and promising energy efficiency (Figure 5).

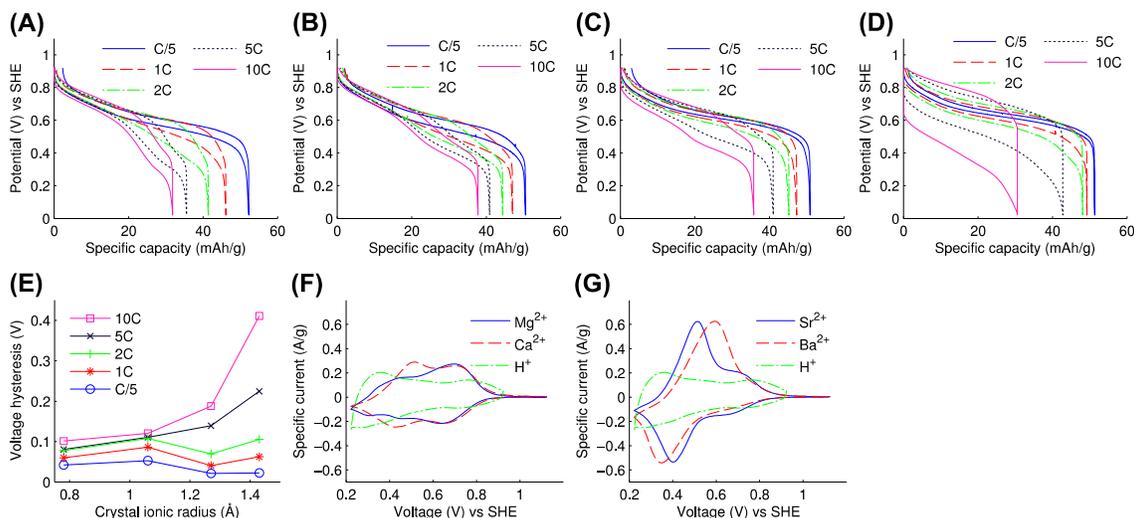


Figure 5. (A–D) Potential profiles of NiHCF upon galvanostatic cycling with Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , respectively, exhibit decreasing capacity and increasing voltage hysteresis with C rate. (E) The voltage hysteresis at half charge increases monotonically with C rate. This increase in hysteresis tends to be greater for cations with larger crystal ionic radii. (F–G) Cyclic voltammetry (CV) curves demonstrate reversible insertion of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , and they suggest two insertion reactions occurring at different potentials.

The present work shows that NiHCF, which has an open framework crystal structure, can also react with divalent insertion cations at high rates to produce unprecedented cycle life and Coulombic and energy efficiencies. The mechanism has not been fully elucidated, but several hypotheses may help explain the observed electrochemical properties

Progress

We have developed new anode materials that match the outstanding properties of the previously reported, open framework hexacyanoferrate cathodes.

By combining these new anodes with copper hexacyanoferrate we have demonstrated new aqueous electrolyte batteries with outstanding electrochemical properties, cycle life and low active materials cost, that make them extremely attractive for grid-related applications, including the smoothing of intermittent variations in power production associated with the integration of renewable energies on the grid.

We have also demonstrated that the PB family of open framework materials not only intercalate monovalent ions but also divalent ions. This opens exciting opportunities to explore a rich variety of intercalations ions for grid scale batteries.

Future Plans

For the remainder of the research project, we plan to carry out the following activities: 1) Study the open framework materials in organic electrolyte, which has potential to increase the voltage of the full batteries. 2) Understand the mechanism of ionic conductivity through in depth electrochemical and crystallographic studies.

Publications and Patents

1. Pasta, M., Wessells, C. D., Huggins, R. A. & Cui, Y. *A high-rate and long cycle life aqueous electrolyte battery for grid-scale energy storage*. Nat. Commun. 3, 1149 (2012).
2. Pasta, M. et al. *Full open-framework batteries for stationary energy storage*. Nat. Commun. 5, 3007 (2014).
3. Wang, R. Y., Wessells, C. D., Huggins, R. A. & Cui, Y. *Highly reversible open framework nanoscale electrodes for divalent ion batteries*. Nano Lett. 13, 5748–52 (2013).

References

None.

Contacts

Yi Cui: yicui@stanford.edu
Robert Huggins: rhuggins@stanford.edu
Richard Wang: ricang@stanford.edu
Mauro Pasta: mpasta@stanford.edu
Hyun Wook Lee: hyunwooklee@stanford.edu