

Safe, Inexpensive, Long Life, High Power Batteries For Use To Support the Electric Grid

Investigators

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Abstract

Grid-scale energy storage calls for low-cost, high power, safe and long cycle life battery chemistry. Built on our previous success in realizing open framework electrodes based on Prussian blue structures, we have made progress in the following area in the past year.

We have demonstrated divalent ion batteries in open framework materials in aqueous solution. In existing batteries, monovalent ion intercalation such as protons and lithium ions into solid materials has led to the success of nickel metal hydride and lithium ion rechargeable batteries. Searching for battery materials for divalent ion interaction is an exciting direction to enable potentially low-cost battery for grid-scale storage. Here we demonstrate that materials in the Prussian Blue (PB) family of open framework materials, such as nickel hexacyanoferrate (NiHCF), can reversibly intercalate aqueous alkaline earth divalent ions: Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} . We show unprecedented long cycle life and high rate performance for divalent intercalation. For example, NiHCF retained 93% of initial capacity after being cycled 2000 times with Ba^{2+} , and the material maintained 96% and 60% of maximum capacity at 1C and 10C, respectively. 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 is aimed 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 PB 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, to reduce the anolyte and catholyte liquid crossing, to improve the ion conducting membrane. One key aspect is related to 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 Aqueion, 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.

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

Results

Give a report of the results from the research project during the past year. This should be the main section of the report. Explain in sufficient technical detail the progress that has been made.

It should be described at a level so that technically adept personnel from our Sponsors will be able to see the progress made. Provide figures to illustrate your results and subheadings as necessary:

Analysis of possibility to intercalation divalent ions

The PB has a general formula of $A_xPR(CN)_6 \cdot yH_2O$, and their crystal structure (Fig. 1a) is analogous to that of the ABX_3 perovskites. The P^{m+} and R^{n+} ions form an ordered arrangement on the B sites. The triple-bonded CN ligands open up the structure for ion and small molecule intercalation. The occupancy of the tetrahedrally coordinated A sites in the large open cages in this crystallographically porous framework (Fig. 1a) varies from $x = 0$ to 2 per formula unit, with corresponding changes in the oxidation states of P and R ions. As a result of these structural characteristics, these materials are mixed ionic and electronic conductors. In addition, zeolitic water in the A sites and on vacant nitrogen sites can facilitate ion intercalation.

We have previously explored PB family materials for monovalent batteries, including potassium and sodium in both aqueous solutions. In particular, both nickel and copper hexacyanoferrate (NiHCF, CuHCF) demonstrate high cycling rates with excellent capacity and cycle life retention. The previous success on monovalent and the large A sites in the crystalline structure makes us believe that divalent ions such as Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} ions can be intercalated for battery application.

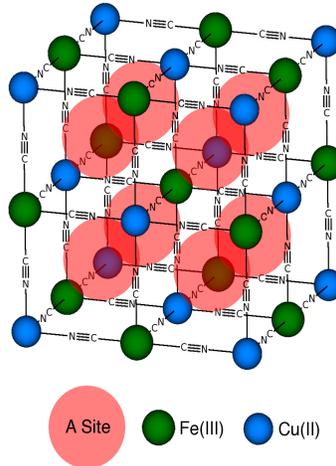


Figure 1: Crystal structure of Prussian Blue (PB) open framework materials.

Electrochemical intercalation divalent ions into open framework materials

NiHCF nanoparticles were synthesized by a coprecipitation method with slow, simultaneous dropwise addition of aqueous nickel nitrate and potassium ferricyanide solutions into deionized water. Their nanoparticles are used to form battery electrodes through slurry coating technique. Fig. 2 shows the galvanostatic cycling data. At C/5, the sloping potential profiles of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} intercalation into NiHCF indicate single-phase intercalation reactions during charge and discharge. This behavior is similar as the case of K^+ and Na^+ intercalation into NiHCF. For Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , the half-charge reaction potentials vs SHE are 0.60 V, 0.59 V, 0.63 V, and 0.64 V, respectively. There is a distinct second plateau in the potential profile at high C rates when the electrodes are discharged beyond roughly 50% of total capacity in Mg^{2+} , Ca^{2+} , or Sr^{2+} . This suggests a two-step intercalation reaction, but the precise mechanism of intercalation for these divalent cations is presently unknown. The retention of specific capacity with increasing charge rate is much higher than previously reported for magnesium electrodes, with retention of specific capacity of 63%, 77%, 70%, and 60% going from C/5 to 10C for Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , respectively.

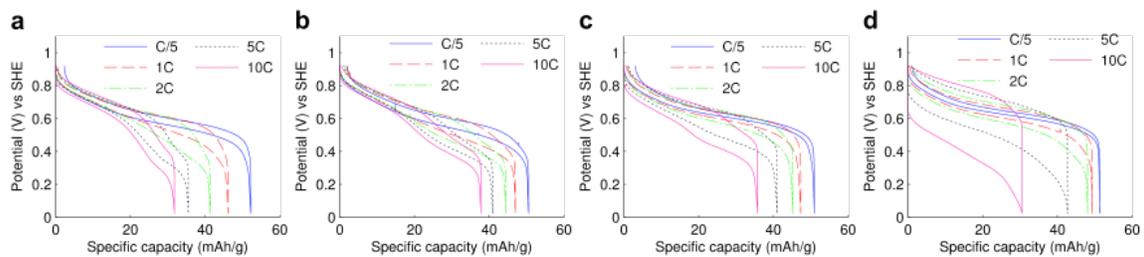


Figure 2: Electrochemical characterization of NiHCF with alkaline earth electrolytes. (a – d) Potential profiles of NiHCF upon galvanostatic cycling with Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , respectively

NiHCF nanoparticles have excellent cycling performance for divalent ions. For example, Figure 3. shows 2000 cycles Ba^{2+} with 93% capacity retention at 5C rate.

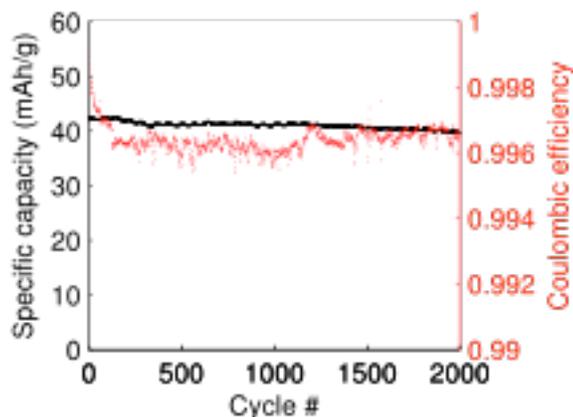


Figure 3: Cycling behavior of NiHCF with Ba²⁺ aqueous electrolyte.

Progress

We have 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. The high power rate, long cycle life and potential for low-cost make this battery chemistry attractive for grid-scale applications. This will ultimately help the integration of wind and solar into electric grid. If the research goals of this project is realized, it has a great potential to reduce greenhouse gas emissions at a global scale.

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) Develop open-framework anodes to match with the existing cathode. Demonstrate the full batteries based on all open-framework materials.

Publications and Patents

1) R. Y. Wang, C. D. Wessells, R. A. Huggins, Y. Cui “Highly Reversible Open Framework Electrodes for Divalent Ion Batteries” (manuscript in review).

References

None.

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