

Nickel Hexacyanoferrate Nanoparticle Electrodes For Aqueous Sodium and Potassium Ion Batteries

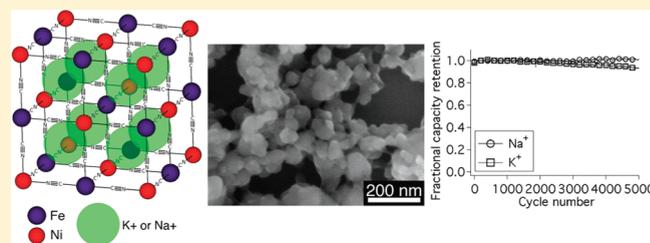
Colin D. Wessells,[†] Sandeep V. Peddada,[†] Robert A. Huggins,[†] and Yi Cui^{*,†,‡}

[†]Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States

[‡]Stanford Institute for Materials & Energy Science, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States

ABSTRACT: The electrical power grid faces a growing need for large-scale energy storage over a wide range of time scales due to costly short-term transients, frequency regulation, and load balancing. The durability, high power, energy efficiency, and low cost needed for grid-scale storage pose substantial challenges for conventional battery technology.^{1,2} Here, we demonstrate insertion/extraction of sodium and potassium ions in a low-strain nickel hexacyanoferrate electrode material for at least five thousand deep cycles at high current densities in inexpensive aqueous electrolytes. Its open-framework structure allows retention of 66% of the initial capacity even at a very high (41.7C) rate. At low current densities, its round trip energy efficiency reaches 99%. This low-cost material is readily synthesized in bulk quantities. The long cycle life, high power, good energy efficiency, safety, and inexpensive production method make nickel hexacyanoferrate an attractive candidate for use in large-scale batteries to support the electrical grid.

KEYWORDS: Energy storage, nickel hexacyanoferrate, Prussian Blue analogue, sodium ion battery, potassium ion battery, aqueous battery



In recent years, research and development of battery technology has primarily been focused on small-scale applications, such as portable electronics and batteries for vehicles, in which the specific energy and energy density are of great importance. These technologies are not widely used for storage capacity in the electric grid,^{1–3} despite costly transient outages,⁴ the rapidly growing need for frequency regulation,⁵ and the necessity for load balancing, particularly in connection with the use of intermittent energy sources such as solar and wind. Traditional grid-scale energy storage systems such as pumped hydropower facilities are location-dependent and suffer from low efficiencies and large capital investment requirements. Storage devices for the grid must have extreme durability (cycle life), high power output, rapid response, and very low cost. No single well-developed battery technology can currently meet all of the requirements for use on the grid; although relatively inexpensive, lead acid batteries have insufficient cycle life and cannot withstand deep discharge, redox-flow batteries have low power densities, and the nickel/metal-hydride and lithium-ion batteries used in portable electronics and vehicles are far too expensive.^{1–3,6} Emerging aqueous lithium and sodium-ion battery systems using inexpensive aqueous electrolytes have shown promising rate capabilities, and in some instances, good cycle life.^{7–9} The recent development of semisolid lithium rechargeable flow batteries also has shown promise.¹⁰

Here, we show that nickel hexacyanoferrate (NiHCF), an analogue of the well-known Prussian Blue coordination compound, can achieve the necessary electrochemical performance in safe,

low-cost aqueous electrolyte cells, making it attractive for practical use in grid-scale batteries. The open framework structure of Prussian Blue and its analogues offers several advantages, including greater durability and faster kinetics when compared to more extensively studied intercalation and displacement battery electrode materials such as carbon, alloys, and metal oxides and oxyfluorides. In this structure (Figure 1a), hexacyanometallate groups ($R(CN)_6$) form a rigid cubic framework with 6-fold nitrogen-coordinated transition metal cations (P, red balls in Figure 1a).^{11–13} Large interstitial sites within the framework may host alkaline ions (A, green balls in Figure 1a) and/or zeolitic water, resulting in a general chemical formula of the form $APR(CN)_6 \cdot (H_2O)_m$. For instance, the Prussian Blue framework is composed of $Fe^{2+}(CN)_6$ and nitrogen-coordinated Fe^{3+} . In the NiHCF material studied here, Ni^{2+} occupies the nitrogen-coordinated lattice sites (Figure 1a), in place of the Fe^{3+} found in Prussian Blue. The relative quantities of A, P, and $R(CN)_6$, and the water content of the structure may vary from unity as the result of defects in the framework. The ion channels connecting the interstitial A sites are similar in size to solvated alkali ions such as potassium, allowing rapid transport of these ions throughout the lattice.^{14,15} Furthermore, electrochemical cycling of these materials over their full composition range results in minimal lattice strain. For these reasons, electrode materials with the Prussian Blue crystal

Received: September 13, 2011

Revised: October 27, 2011

Published: November 01, 2011

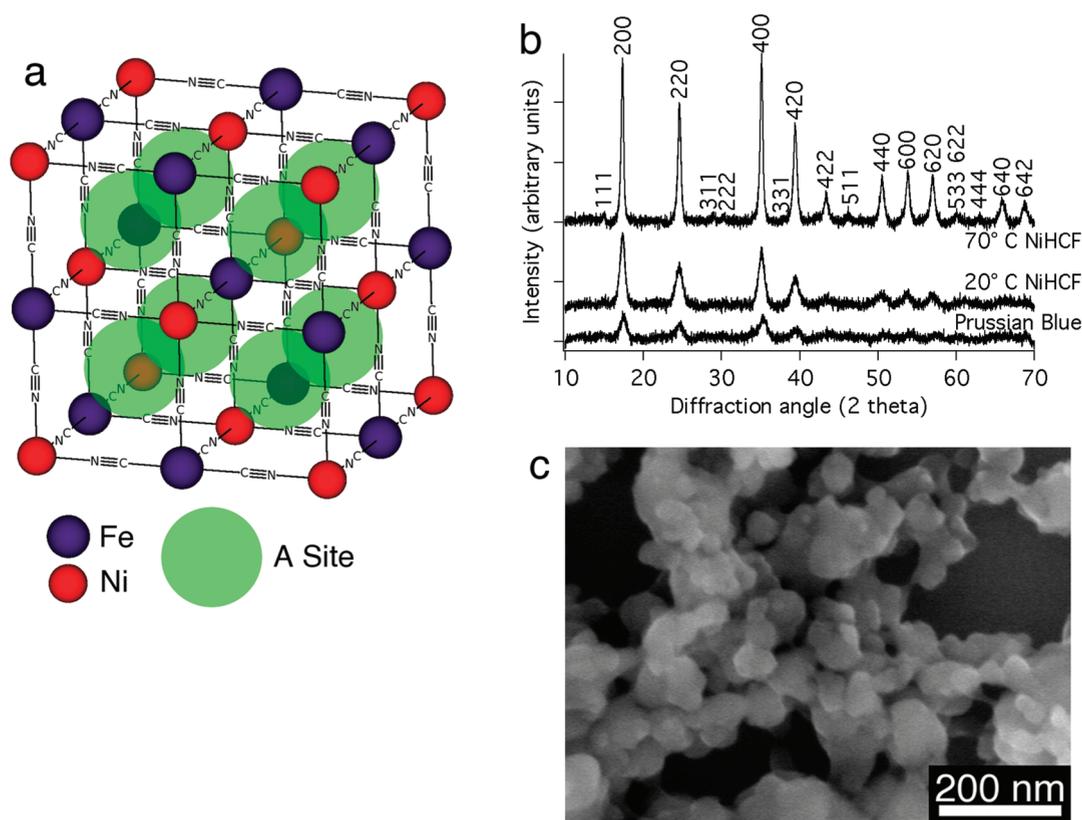


Figure 1. (a) NiHCF has the Prussian Blue crystal structure in which transition metal cations such as Fe and Ni are bound by bridging CN ligands, forming a face-centered cubic structure. In the case of NiHCF, Fe is 6-fold carbon coordinated, while Ni is 6-fold nitrogen coordinated. The resulting framework has large channels oriented in the $\langle 100 \rangle$ directions, through which hydrated alkaline cations such as K^+ and Na^+ may diffuse. These alkaline cations occupy the interstitial “A” sites at the center of each of the eight subcells of the unit cell. Full occupancy of the A sites is achieved upon full reduction of the material to $A_2NiFe^{2+}(CN)_6$. Zeolitic water is also present in the structure but is omitted here for clarity. (b) Powder X-ray diffraction showed that synthesis of NiHCF at 70 °C produced higher crystallinity than a synthesis at room temperature. (c) Scanning electron microscopy revealed that the as-synthesized NiHCF powder is composed of a porous collection of 20–50 nm grains.

structure can show stable cycling over many thousands of cycles with extremely high rate capability.^{15,16}

Coordination compounds such as Prussian Blue analogues and a variety of metal–organic framework materials have tunable, open structures that allow insertion of both molecular and ionic species, which has led to their study for applications including hydrogen storage, battery electrodes, and electrochromics.^{17–19} In addition, Prussian Blue analogues have received significant attention for their magnetic properties.^{20–22} The electrochemical activity of Prussian Blue was first demonstrated by Neff,²³ and electrochromic devices using very thin films (40–300 nm) of Prussian Blue have shown lifetimes on the order of 10^6 cycles during extremely rapid cycling (up to 1 Hz).^{15,16} During this epoch, electrochemical cycling of analogous materials, such as NiHCF, was also reported.^{24–27} The electrochemical reaction of NiHCF may be described by the following expression: $ANiFe^{3+}(CN)_6 + A^+ + e^- = A_2NiFe^{2+}(CN)_6$, where A^+ is an alkali ion, such as sodium or potassium. However, previous electrochemical studies have been carried out only on very thin electrodeposited films with thicknesses of approximately 100 nm, too thin for practical batteries.^{25–27} This report is the first to describe a rechargeable NiHCF electrode on the size scale ($\sim 10 \text{ mg/cm}^2$) relevant to real batteries.

Bulk syntheses of Prussian Blue and its analogues have long been performed by spontaneous precipitation methods.^{11–13} Aqueous

solutions of iron salts such as $FeCl_3$ are typically combined with a solution of $K_4Fe^{2+}(CN)_6$, resulting in the rapid precipitation of solid $KFe^3Fe^{2+}(CN)_6$. The extreme insolubility of Prussian Blue hinders the control of its crystallinity and composition during precipitation.¹² In this work, NiHCF was synthesized by a coprecipitation method that ensured consistent reaction conditions. Slow, simultaneous dropwise addition of aqueous precursors to a common liquor maintains a constant ratio of reactants, ensuring a consistent composition of precipitate. In a typical synthesis, aqueous precursors containing $Ni(NO_3)_2$ and $K_3Fe(CN)_6$ were reacted by simultaneous dropwise addition into pure water with final concentrations of 40 and 20 mM, respectively. The solid precipitate was filtered, washed with water, and dried in vacuum at room temperature. Elemental analysis of the precipitate using inductively coupled plasma mass spectroscopy, along with previous conventions for the water content of the Prussian Blue structure,¹² showed that NiHCF may be described by the formula $K_{0.6}Ni_{1.2}Fe(CN)_6 \cdot 3.6H_2O$. Precipitation of Prussian Blue occurs too rapidly to yield a well-crystallized product, even under these controlled reaction conditions. The syntheses of NiHCF were performed at 70 °C to improve crystallinity. Highly crystalline, nanoparticulate (20–50 nm) NiHCF may be formed using this method, as shown by powder X-ray diffraction (XRD) (Figure 1b) and scanning electron microscopy (SEM) (Figure 1c). The resulting porous agglomerations

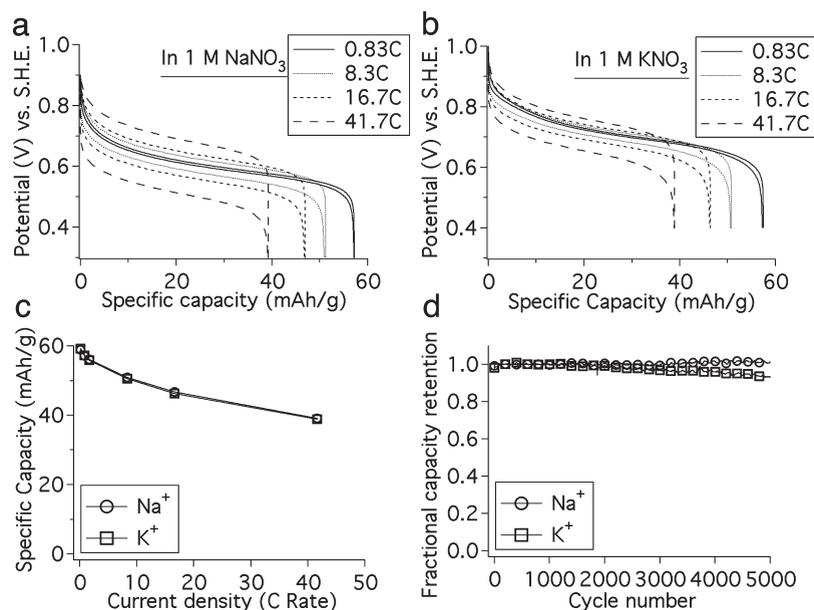


Figure 2. (a,b) The potential profiles of NiHCF during galvanostatic cycling of Na⁺ and K⁺ at various rates are shown. The potential profiles during both Na⁺ and K⁺ cycling show that the reversible reduction of fully charged NiHCF proceeds by an insertion reaction, during which both Na⁺ and K⁺ are miscible over a wide composition range in the stable metal–organic framework structure. Specific capacities of 59 mAh/g were observed at a C/6 rate (panel c, omitted from panels a and b for clarity), so 60 mA/g was defined as a 1C rate. (c) The capacity of NiHCF during galvanostatic cycling of Na⁺ and K⁺ at various rates is shown. Two thirds of the capacity observed at a C/6 rate is retained at 41.7C. (d) NiHCF shows no capacity loss after 5000 cycles of Na⁺ insertion at a 8.3C rate. However, during K⁺ cycling, NiHCF is stable for only about 1000 cycles, after which its capacity decays at an approximate rate of 1.75%/1000 cycles.

of NiHCF nanoparticles allow for rapid transport of charge carriers throughout electrodes containing NiHCF.

Electrodes containing NiHCF were prepared by combining NiHCF, amorphous carbon (Timcal SuperP Li), polyvinylidene difluoride (Kynar HSV900), and graphite (Timcal KS6) in a 80:9:9:2 ratio. These materials were ground together by hand and then dispersed in a slurry of 1-methyl-2-pyrrolidinone. Slurries were deposited on carbon cloth (Fuel Cell Earth, Inc.) and dried in vacuum at 80 °C. The mass loading of electrodes was between 7 and 12 mg NiHCF/cm². Electrochemical cycling of electrodes containing NiHCF powder was performed in aqueous, mildly acidic 1 M NaNO₃ or 1 M KNO₃. Electrolytes were acidified to pH = 2 by adding dilute nitric acid. Measurements on NiHCF were performed using three-electrode flooded cells containing a Ag/AgCl reference electrode and a counter electrode containing a large, partially discharged mass of NiHCF. This counter electrode acted as a reversible ion sink, similar to the large masses of lithium foil typically used during half-cell tests of lithium ion electrodes. The as-synthesized NiHCF is fully oxidized with a high open circuit voltage. However, to avoid any potassium contamination during experiments in the sodium electrolyte, all mobile cations were removed from the counter electrodes by fixing their potentials at 1.0 V versus the standard hydrogen electrode (SHE) for 30 min in fresh sodium electrolyte. After washing with water, they were then partially discharged in fresh electrolyte by fixing their potential at the half-discharge potential of NiHCF.

NiHCF was found to react with sodium at 0.59 V versus the SHE, while its reaction with potassium occurs at 0.69 V (Figure 2a,b). The trend to higher reaction potentials for the insertion of heavier alkaline ions corroborates previous observations on Prussian Blue and NiHCF.^{25,28} The theoretical specific

capacity of NiHCF and other Prussian Blue analogues is about 60 mAh/g, but its exact value is difficult to determine because the zeolitic water content varies with temperature and humidity. The theoretical capacities of these materials can also vary by ten percent or more, depending on the concentration of defects in the framework structure. For this study, a current density of 60 mA/g is defined as 1C.

The open framework structure and nanoparticulate morphology of NiHCF allow for rapid kinetics during the cycling of both sodium and potassium. During either sodium or potassium cycling, a specific capacity of 59 mAh/g was observed at a C/6 rate (Figure 2a,b). Virtually all of this capacity is accessible within a narrow 0.3 V range around the half-charge reaction potential. Recently reported work on another sodium insertion material, Na₄Mn₉O₁₈, showed a maximum discharge capacity of 45 mAh/g over a wider, 0.5 V, range.⁹ To the authors' knowledge, the only previously demonstrated potassium ion electrodes for aqueous cells are other Prussian Blue analogues, thin films of which have specific capacities similar to that of NiHCF.

During sodium cycling of NiHCF, the rate performance is excellent (Figure 2c), as 86.5% of its maximum low rate capacity is retained at a rate of 8.3C, and 67% is retained at a very high 41.7C rate. NiHCF behaves similarly during potassium cycling: 85.5% of its maximum capacity is retained at 8.3C, and 66% is retained at 41.7C. In contrast, Na₄Mn₉O₁₈ was reported to lose more than half of its discharge capacity when operated at a 18C rate.⁹ The high rate performance of NiHCF corroborates the extremely rapid cycling of thin film Prussian Blue electrochromic devices.¹⁵ The capacity retention of NiHCF at high-current densities is comparable to the best rate performance of any known lithium-ion electrode material. For example, over a wide one-volt cycling window between 3.0 and 4.0 V versus Li⁺/Li,

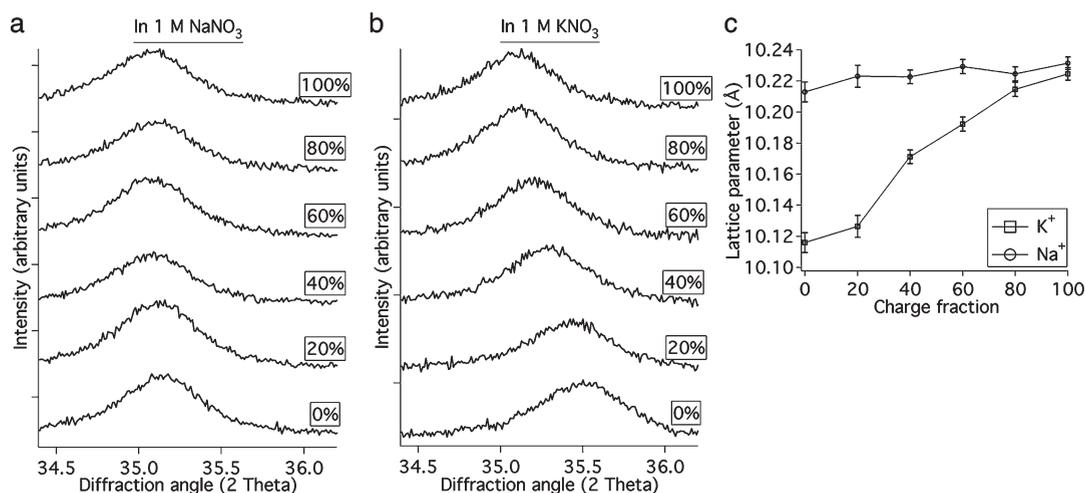


Figure 3. Ex-situ XRD experiments on NiHCF at various charge states showed isotropic lattice strain during charging. (a,b) Changes in the diffraction pattern are illustrated by the shift of the 400 diffraction peak to lower angles with increasing charge state. (c) The lattice parameter increases approximately linearly with charge state with total strains of 0.18 and 1.1% during full Na^+ and K^+ insertion, respectively.

LiFePO_4 , a common lithium ion cathode reactant, has been shown to retain approximately 70% of its theoretical capacity at a 20C rate.^{29,30}

NiHCF has unusually low voltage hysteresis between charge and discharge during either sodium or potassium cycling (Figure 2a,b). The low voltage hysteresis is due to its open framework structure and the fast ionic diffusion within it. In our experiments the voltage hysteresis of NiHCF at a half-charged state during sodium cycling was only 12.7 mV at 0.83C, (about $0.4 \text{ mA}/\text{cm}^2$). At the same current density in a potassium electrolyte, the half-charge voltage hysteresis of NiHCF was less, only 8 mV. The voltage hysteresis increased linearly with current density, and during 41.7C cycling (about $18 \text{ mA}/\text{cm}^2$), it reached 178 mV during sodium cycling, and 106 mV during potassium cycling. The ohmic behavior of the voltage hysteresis clearly resulted from the flooded cell geometry, in which much of the total impedance of the cell was due to electrolyte resistance. The difference between the voltage hystereses during cycling of sodium and potassium probably arose from variations in cell geometry. The use of compressed cells in future studies will make even lower voltage hystereses possible.

The low voltage hysteresis of NiHCF allows it to achieve higher energy efficiency than conventional battery electrodes. Round trip energy efficiency also depends on Coulombic efficiency, and the Coulombic efficiency of NiHCF was between 99.7 and 99.9% during cycling. Thus, only the voltage hysteresis of NiHCF has a non-negligible effect on its energy efficiency. In a hypothetical cell of nominal voltage of 1.0 V that contains NiHCF and a perfectly reversible counter electrode, the round trip energy efficiency is 98–99% at a 0.83C rate. At higher current densities, an energy efficiency of 90% is attained during potassium cycling at the very high rate of 41.7C, and an efficiency of 83% during sodium cycling at the same rate. The energy efficiency of full cells using NiHCF electrodes will be even higher with a pressed cell geometry, but they already surpass conventional batteries: a typical efficiency for lead acid and vanadium flow batteries is 75%, while only at low current densities can lithium ion batteries achieve efficiencies above 90%.^{1,2}

NiHCF shows complete reversibility during electrochemical cycling of sodium with zero capacity loss after 5000 cycles at a

8.3C rate (Figure 2d). In addition, there is no capacity loss during the cycling of potassium for the first 1000 cycles, after which capacity is lost at a rate of 1.75%/1000 cycles. In comparison, the $\text{Na}_4\text{Mn}_9\text{O}_{18}$ sodium electrode was shown to maintain stable capacity during cycling for only 1000 cycles.⁹ A more-recently reported sodium-ion electrode material, $\text{NaTi}_2(\text{PO}_4)_3$, suffered severe capacity loss in 30 cycles in an aqueous electrolyte.³¹ Among conventional battery systems, lead acid cells typically last about one thousand cycles during 50% discharge capacity cycling, and the best vanadium redox flow cells last up to 5000 cycles at 70% discharge.^{1,3,32}

The rigid metal–organic framework of the Prussian Blue structure provides the structural and chemical stability that allows NiHCF to repeatedly cycle sodium and potassium ions with stable capacities. As stated above, physical characterization of NiHCF produced by the coprecipitation method using SEM and XRD revealed a porous, nanostructured morphology with high crystallinity. The as-synthesized NiHCF powder was found to have an XRD spectrum corresponding to a phase-pure face-centered cubic structure with a lattice parameter of 10.2 Å (Figure 1b).

To examine the effect of charge state on the NiHCF structure, ex-situ XRD spectra of NiHCF electrodes were measured at several different charge states. To prepare the electrodes, they were first fully cycled ten times at 250 mA/g, ending at full discharge. The electrodes were then charged to the desired fractional charge state at the same current density. The necessary duration of the final charging current was determined from the specific capacity of each electrode observed during the initial ten cycles. Ex-situ XRD spectra of the electrodes at different states of charge reveals that the lattice parameter increases during charging (cation extraction), as illustrated by a shift in the position of the 400 diffraction peak to smaller angles (Figure 3a,b). The isotropic lattice strain reaches a maximum of 1.1% during potassium cycling, but only 0.18% during sodium cycling (Figure 3c), which correlates with the better cycle life during sodium cycling. The reported lattice parameters are the average of the lattice parameters determined from at least six diffraction peaks for each sample, and the error bars in Figure 3c represent one standard deviation from the mean calculated lattice

parameter of each sample. The small increase in lattice parameter during charging corresponds to an increase in the radius of $[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ ions during their oxidation to $[\text{Fe}^{3+}(\text{CN})_6]^{3-}$.³³ The difference in the magnitudes of the lattice strain during the insertion of potassium and sodium is not yet well understood. As noted during early research on Prussian Blue films, the radius of the channel between the A sites in the Prussian Blue structure is comparable to the Stokes radius of hydrated potassium, but significantly smaller than the Stokes radius of hydrated sodium.¹⁵ The possibility that the water molecules in the hydration shells of potassium and sodium might exchange with zeolitic water already present in the crystal structure further complicates the understanding of the mechanism involved in ion transport through the lattice.

The NiHCF material studied here was synthesized in bulk quantities using spontaneous chemical coprecipitation from relatively low-purity aqueous precursors at modest temperatures. Such a synthesis method is both scalable and inexpensive. In addition, Prussian Blue analogues such as NiHCF operate in safe, inexpensive aqueous electrolytes, and possess superior rate capability, round trip energy efficiency, and cycle life. Together, these characteristics make them especially desirable for energy storage to support the electrical energy grid.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yicui@stanford.edu.

ACKNOWLEDGMENT

The authors acknowledge support from the King Abdullah University of Science and Technology (KAUST) Investigator Award (No. KUS-I1-001-12). A portion of this work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under contract DE-AC02-76SF00515 through the SLAC National Accelerator Laboratory LDRD project.

REFERENCES

- (1) Yang, Z.; et al. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **2011**, *111* (5), 3577–3613.
- (2) Barton, J. P.; Infield, D. G. Energy Storage and its Use With Intermittent Renewable Energy. *IEEE Trans. Energy Convers.* **2004**, *19*, 441.
- (3) Soloveichik, G. L. Battery technologies for large-scale energy storage. *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2* (22), 1–22.25.
- (4) LaCommare, K. H.; Eto, J. H. Understanding the cost of power interruptions to the U.S. electricity consumers. DOE Environmental Energy Technologies Division. *LBLN-5518* **2004**.
- (5) Makarov, Y. V.; Loutan, C.; Ma, J.; de Mello, P. Operational impacts of wind generation on California power systems. *IEEE Trans. Power Syst.* **2009**, *24*, 1039.
- (6) Howell, D. Energy Storage and Development. United States Department of Energy: Washington, DC, 2008.
- (7) Ruffo, R.; Wessells, C.; Huggins, R. A.; Cui, Y. Electrochemical behavior of LiCoO_2 as aqueous lithium-ion battery electrodes. *Electrochem. Commun.* **2009**, *11*, 247.
- (8) Luo, J.-Y.; Cui, W.-J.; He, P.; Xia, Y.-Y. Raising the cycling stability of aqueous lithium-ion batteries by eliminating oxygen in the electrolyte. *Nature Chem.* **2010**, *2*, 760.
- (9) Whitacre, J. F.; Tevar, A.; Sharma, S. $\text{Na}_4\text{Mn}_9\text{O}_{18}$ as a positive electrode material for an aqueous electrolyte sodium-ion energy storage device. *Electrochem. Commun.* **2010**, *12*, 463.
- (10) Duduta, M.; et al. Semi-Solid Lithium Rechargeable Flow Battery. *Adv. Energy Mater.* **2011**, *1*, 511.
- (11) Ludi, A.; Güdel, H. U. Structural chemistry of polynuclear transition metal cyanides. *Struct. Bonding (Berlin)* **1973**, *14*, 1.
- (12) Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. The crystal structure of Prussian Blue: $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$. *Inorg. Chem.* **1977**, *16*, 2704.
- (13) Herren, F.; Fischer, P.; Ludi, A.; Halg, W. Neutron diffraction study of Prussian Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$. Location of Water Molecules and Long-Rate Magnetic Order. *Inorg. Chem.* **1980**, *19*, 956.
- (14) Itaya, K.; Ataka, T.; Toshima, S. Spectroelectrochemistry and Electrochemical Preparation Method of Prussian Blue Modified Electrodes. *J. Am. Chem. Soc.* **1982**, *104*, 4767.
- (15) Stilwell, D. E.; Park, K. H.; Miles, M. H. Electrochemical studies of the factors influencing the cycle stability of Prussian Blue films. *J. Appl. Electrochem.* **1992**, *22*, 325.
- (16) Oi, T. Electrochromic Materials. *Annu. Rev. Mater. Sci.* **1986**, *16*, 185.
- (17) Rosi, N. L.; et al. Hydrogen Storage in Microporous Metal-Organic Frameworks. *Science* **2003**, *300*, 1129.
- (18) Dinca, M.; et al. Hydrogen Storage in a Microporous Metal-Organic Framework with exposed Mn^{2+} Coordination Sites. *J. Am. Chem. Soc.* **2006**, *128*, 16876.
- (19) Férey, G.; et al. Mixed-valence Li/Fe-based metal-organic frameworks with both reversible redox and sorption properties. *Angew. Chem., Int. Ed.* **2007**, *46*, 3259.
- (20) Entley, W. R.; Girolami, G. S. High-Temperature Molecular Magnets Based on Cyanovanadate Building Blocks: Spontaneous Magnetization at 230 K. *Science* **1995**, *268*, 397.
- (21) Juszczuk, S.; Johansson, C.; Hanson, M.; Ratuszna, A.; Malecki, G. Ferrimagnetism of the $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$ compounds, where Me = Ni and Co. *J. Phys.: Condens. Matter* **1994**, *6*, S697.
- (22) Hashimoto, K.; Ohkoshi, S.-I. Design of novel magnets using Prussian blue analogues. *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 2977.
- (23) Neff, V. D. Electrochemical oxidation and reduction of thin films of Prussian Blue. *J. Electrochem. Soc.* **1978**, *125*, 886.
- (24) Itaya, K.; Uchida, I.; Neff, V. D. Electrochemistry of Polynuclear Transition Metal Cyanides: Prussian Blue and its Analogues. *Acc. Chem. Res.* **1986**, *19*, 162.
- (25) Bocarsly, A. B.; Sinha, S. Effects of Surface Structure on Electrode Charge Transfer Properties: Induction of Ion Selectivity at the Chemically Derivatized Interface. *J. Electroanal. Chem.* **1982**, *140*, 167.
- (26) Sinha, S.; Humphrey, B. D.; Bocarsly, A. B. Reaction of Nickel Electrode Surfaces with Anionic Metal-Cyanide Complexes: Formation of Precipitated Surfaces. *Inorg. Chem.* **1984**, *23*, 203.
- (27) Kalwellis-Mohn, S.; Grabner, E. W. A Secondary Cell Based on Thin Layers of Zeolite-like Nickel Hexacyanometallates. *Electrochem. Acta* **1989**, *34*, 1265.
- (28) McCargar, J. W.; Neff, V. D. Thermodynamics of mixed-valence intercalation reactions: the electrochemical reduction of Prussian Blue. *J. Phys. Chem.* **1988**, *92*, 3598.
- (29) Kang, B.; Ceder, G. Battery materials for ultrafast charging and discharging. *Nature* **2009**, *458*, 190.
- (30) Ceder, G.; Kang, B. Response to “unsupported claims of ultrafast charging of Li-ion batteries..” *J. Power Sources* **2009**, *194*, 1024.
- (31) Park, S. I.; Gocheva, I.; Okada, S.; Yamaki, J.-i. Electrochemical Properties of $\text{NaTi}_2(\text{PO}_4)_3$ Anode for Rechargeable Aqueous Sodium-Ion Batteries. *J. Electrochem. Soc.* **2011**, *158*, A1067.
- (32) Schreiber, M. Vanadium Redox Flow Batteries in der Anwendung. Presentation at VDI Conference. Wiesbaden, Germany, May, 2011.
- (33) Dostal, A.; Kauschka, G.; Reddy, S. J.; Scholz, F. Lattice contractions and expansions accompanying the electrochemical conversions of Prussian Blue and the reversible and irreversible insertion of rubidium and thallium ions. *J. Electroanal. Chem.* **1996**, *406*, 155.