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Short communication

High performance Prussian Blue cathode for nonaqueous Ca-ion intercalation battery

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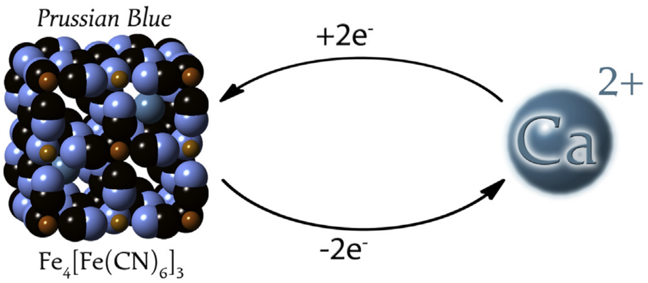
HIGHLIGHTS

- Iron Hexacyanoferrate, Prussian Blue, is shown to reversibly intercalation Ca-ions.
- Prussian Blue is shown to be a suitable cathode for nonaqueous Ca-ion batteries.
- Prussian Blue exhibits the highest reversible capacity for a Ca-ion battery to date.
- Prussian Blue shows good rate capability and low capacity fading over many cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Potassium iron hexacyanoferrate, or Prussian blue (PB), is investigated as a cathode material for nonaqueous divalent calcium ion batteries. PB is an attractive prospect due to its high specific capacity, nontoxicity, low cost, and simple synthesis. Charge/discharge performances are examined at current densities of 23 mAg^{-1}, 45 mAg^{-1}, 90 mAg^{-1}, and 125 mAg^{-1} that produced reversible specific capacities ranging from 150 $mAhg^{-1}$ (at 23 mAg^{-1} current density) to over 120 $mAhg^{-1}$ (at 125 mAg^{-1} current density). These are the highest storage capacities to date for a divalent calcium ion cathode over extended period of charge/discharge cycling and are comparable in performance to monovalent intercalating ions.

1. Introduction

Divalent ions have been of interest for rechargeable batteries for many years owing to the fact that a doubly charged ion can accept two electrons for a single ion. For intercalation type batteries, this means fewer ions would need to diffuse into a lattice for a given capacity, which could result in less severe lattice distortion and more reliable cells. The most interesting candidates for multivalent ion cells are Be^{2+}, Mg^{2+}, and Ca^{2+} (and Al^{3+} if trivalent ions are included) due to their lightweight and small ionic radii. Be^{2+} can be excluded as a candidate for multivalent ion batteries due to its rarity and toxicity. Of the remaining ions, Ca^{2+} has the highest potential, and is very close to that of Li+ (−2.87 V vs SHE compared to −3.04 V for Li). This makes Ca-ions a very attractive guest species for intercalation type batteries. Early work on Ca^{2+} cells, however, showed that Ca metal electrodes in nonaqueous electrolytes formed a surface passivation layer that inhibited electron transfer

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[1–4].

Intercalation electrodes are attractive for Ca-ion batteries, where the Ca ions are not plated during discharging, but inserted into the cathode lattice followed by reduction of lattice ions. Amatucci et al. and Hayashi et al. studied the electrochemical insertion and extraction of calcium into nanocrystalline V_2O_5 [5] and V_2O_5 nanocomposites [3,6] while demonstrating high specific capacities, 200 $mAhg^{-1}$, 400 $mAhg^{-1}$, and 465 $mAhg^{-1}$ respectively, for a maximum of ten cycles. Very recently, a reversible capacity of 100 $mAhg^{-1}$ was achieved using a $CaCo_2O_4$ cathode in a completely nonaqueous system [7].

Prussian blue analogs ($A_xMFe(CN)_6 \cdot nH_2O$ where A is an alkali metal or alkaline earth metal, and M is a transition metal; abbreviated PBA) have also been investigated as intercalation based cathode materials for calcium ion batteries. $NiFe(CN)_6$ [8] was used as a cathode in an aqueous system and exhibited a capacity of 50 $mAhg^{-1}$, while in mixed solvent aqueous electrolytes $CoFe(CN)_6$ [9] and $BaFe(CN)_6$ [10] delivered capacities of 82 $mAhg^{-1}$ and 55 mAhg-1 respectively. Several completely nonaqoues systems with PBA cathodes have been studied, which include $CoFe(CN)_6$ [11], $NiFe(CN)_6$ [11,12], and $MnFe(CN)_6$ [13,14] cathodes with maximum reversible capacities of 20 $mAhg^{-1}$, 60 $mAhg^{-1}$, and 110 $mAhg^{-1}$ respectively. PBA cathodes have shown good capacity retention over a large number of cycles. Only the maximum values reported in literature are listed above. In this work, we report our initial results of the performance of iron hexacyanoferrate, or Prussian blue, cathodes with Ca-ions in a nonaqueous acetonitrile (AN) electrolyte.

2. Materials and methods

PB ($KFe^{3+}(Fe^{2+}(CN)_6)$) was synthesized using the same procedure as we have previously reported [15]. Briefly, the PB was synthesized at 60 °C by slowly adding 0.05 M ferric nitrate in 25 mL deionized (DI) water to 0.1 M potassium ferrocyanide in 25 mL DI water, under constant stirring. The blue precipitate was stirred for 2 h, followed by cleaning via centrifugation at 7000 rpm with DI water and ethanol. The precipitate was dried in an oven at 60 °C and then annealed at 150 °C under vacuum for 24 h to reduce the water content of the material.

PB cathodes were prepared by combining annealed PB powder with polyvinylidene fluoride (PVDF) which served as a binder, and multi-walled carbon nanotubes and activated carbon as conductivity enhancers in the ratio of 80:9:9:2, respectively by weight. The electrode mixture was ground using a mortar and pestle until a fine powder was achieved and then mixed with *N*-methyl-2-pyrolidone (NMP) to form a paste. The paste was applied onto rectangular pieces of carbon paper and dried for 2 h at 150 °C under vacuum. After cooling, the electrodes were weighed to determine the amount of active material present. The finished PB cathodes (total weight on the order of 1 mg of active material, surface area 4 cm^2) were weighed on an analytical balance with precision to ± 0.1 mg, and confirmed on another analytical balance of similar precision.

All electrochemical measurements were carried out on a Princeton Applied Research 273a potentiostat. The PB cathodes were characterized using cyclic voltammetry (CV) and galvanic cycling in a 3-electrode setup with a graphite rod as a counter electrode and an Ag/Ag^+ reference electrode in a 1 M $AgNO_3$/dry AN electrolyte. A ferrocene redox (Fc/Fc^+) reference was used in the electrolyte to calibrate the Ag/Ag^+ potential. The solvent used in all tests was acetonitrile which was dried prior to use by passing through a column of molecular sieves. Both the potassium (KPF_6 in dry AN) and calcium ($Ca(ClO_4)_2 \cdot xH_2O$ in dry AN) electrolytes were left over 3 Å molecular sieves overnight to eliminate water. Once a cell was assembled, argon was flowed in the headspace and molecular sieves were placed in the bottom of the three electrode cells to limit any additional water absorption. All sieves were activated prior to use by heating at 150 °C in an oven overnight.

The crystallographic structure of the annealed PB powder was characterized using powder X-ray diffraction (XRD) performed on a Rigaku Ultima IV X-ray diffractometer with CuKα radiation. Indexing and Rietveld refinement were conducted using the Fullprof crystallographic suite [16]. Morphology and particle size was investigated through scanning electron microscopy using a FEI Sirion XL30 scanning electron microscope (SEM). Elemental content of the PB cathodes was detected using energy dispersive x-ray spectroscopy (EDX) on an Oxford Instruments EDX detector mounted on the Sirion SEM.

3. Results and discussion

Song et al. have shown that removal of interstitial water by annealing under vacuum leads to superior electrochemical and battery performance, as well as possible structural distortions [17]. Heating Prussian blue to 150 °C eliminates most of the water from the material [11,18]. To confirm Prussian blue's structural stability at 150 °C, XRD measurements were performed before and after annealing (Fig. S1). The XRD patterns show no noticeable changes, indicating the material did not undergo any detectable structural changes. The annealed Prussian Blue is confirmed to have a cubic crystal structure using powder x-ray diffraction with a lattice parameter of 10.21 Å and space group Pm3m (Fig. S2). The XRD spectrum displays sharp and well defined peaks indicating good crystallinity in the sample. The SEM images affirm the good crystallinity and show cubic particles ranging between 20 nm and 200 nm (Fig. S3).

All electrochemical measurements of PB cathodes were performed in a three electrode system as described in the materials and methods. Fig. S4 shows the cyclic voltammetry (CV) for PB with $Ca(ClO_4)_2$ in dry AN with the ferrocene reference added to the electrolyte. For our system, the measured potential offset is 68 mV for Ag/Ag^+, which was then added to all measurements to plot voltages with reference to Fc/Fc^+. The ferrocene redox potential is roughly 2.8 V against Ca/Ca^+ as reported by Lipson et al. [13].

The nonaqueous potassium electrolyte (KPF_6/dry AN) is used as a benchmark to verify the performance of the PB cathode. Fig. 1a shows the CV for PB in the 1M KPF_6 based electrolyte. Two well defined redox pairs are observed at 0.67 V and 0.44 V, and 0.01 V and −0.18 V corresponding to both Fe ions switching oxidation states. An unidentified third anodic peak is observed in the KPF_6 electrolyte at −0.24 V and remains for all subsequent CV tests. A similar peak also occurs when cycling the Ca-ion electrolyte and is reported by others [13]. The origin of the peak needs further exploration.

The electrochemical properties of PB upon intercalation and deintercalation of Ca^{2+} were examined using the same cell geometry as for potassium, but with 1M $Ca(ClO_4)_2$ in dry AN. The cyclic voltammogram for Ca^{2+} is shown in Fig. 1b. Unlike with K^+, the redox peaks of PB with Ca-ions are broad and less distinguishable. This is likely a result of higher resistance to intercalation/deintercation of Ca-ions. The undetermined anodic peak was present again.

To determine if the new anodic peak is due to a reaction with the PB cathode, cyclic voltammetry measurements of a symmetric carbon-carbon cell with $Ca(ClO_4)_2$ in dry acetonitrile were conducted (Fig. S5). Despite the absence of any PB, the peak is present. The source of the peak thus does not originate from any reaction with PB, but could possibly be attributed to formation of a surface electrolyte interphase at the anode, electrolyte decomposition, or an unknown anodic reaction.