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Nickel hexacyanoferrate, a versatile intercalation host for divalent ions from nonaqueous electrolytes

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HIGHLIGHTS

- Nickel hexacyanoferrate is shown to electrochemically insert Mg, Ca and Zn ions.
- Intercalation voltages are 2.9 V, 2.6 V, and 1.2 V for Mg, Ca and Zn, respectively.
- Changes to composition, structure, and iron oxidation state are observed.
- The electrochemistry is reversible.

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ABSTRACT

New energy storage chemistries based on Mg ions or Ca ions can theoretically improve both the energy density and reduce the costs of batteries. To date there has been limited progress in implementing these systems due to the challenge of finding a high voltage high capacity cathode that is compatible with an electrolyte that can plate and strip the elemental metal. In order to accelerate the discovery of such a system, model systems are needed that alleviate some of the issues of incompatibility. This report demonstrates the ability of nickel hexacyanoferrate to electrochemically intercalate Mg, Ca and Zn ions from a nonaqueous electrolyte. This material has a relatively high insertion potential and low overpotential in the electrolytes used in this study. Furthermore, since it is not an oxide based cathode it should be able to resist attack by corrosive electrolytes such as the chloride containing electrolytes that are often used to plate and strip magnesium. This makes it an excellent cathode for use in developing and understanding the complex electrochemistry of multivalent ion batteries.

1. Introduction

After many years of research, electric vehicles and grid storage are starting to be deployed using Li-ion batteries; however, mass market penetration has not been realized due to issues related to their cost, lifetime, and energy density. There are many possible avenues to reduce the cost of batteries, such as increasing the capacity and reducing the cost of raw materials [1]. By using a multivalent working ion, such as Mg or Ca, a battery with higher capacity and lower cost materials could potentially be made. In particular, these multivalent elements are substantially more abundant in the earth's crust as compared to Li, which results in them being considerably less expensive. Additionally, these systems can be designed to utilize a metal anode, which dramatically increases the capacity of the cell relative to the use of an intercalation host anode (e.g., graphite), thereby further reducing the system cost. Li-metal anodes have been explored for decades; however, there are still substantial challenges to commercialization related to dendrite formation, low coulombic efficiency, and high reactivity [2]. Mg metal anodes, on the other hand, are achievable and show improved plating properties relative to Li-metal [3]. Ultimately, Mg and other multivalent ions are predicted to provide a significant increase in volumetric energy density and reduction in cost relative to Li-ion technologies [4].

A successful rechargeable mutivalent battery requires a high capacity cathode that can support reasonable cycling rates. Many cathode materials for Mg intercalation have been explored

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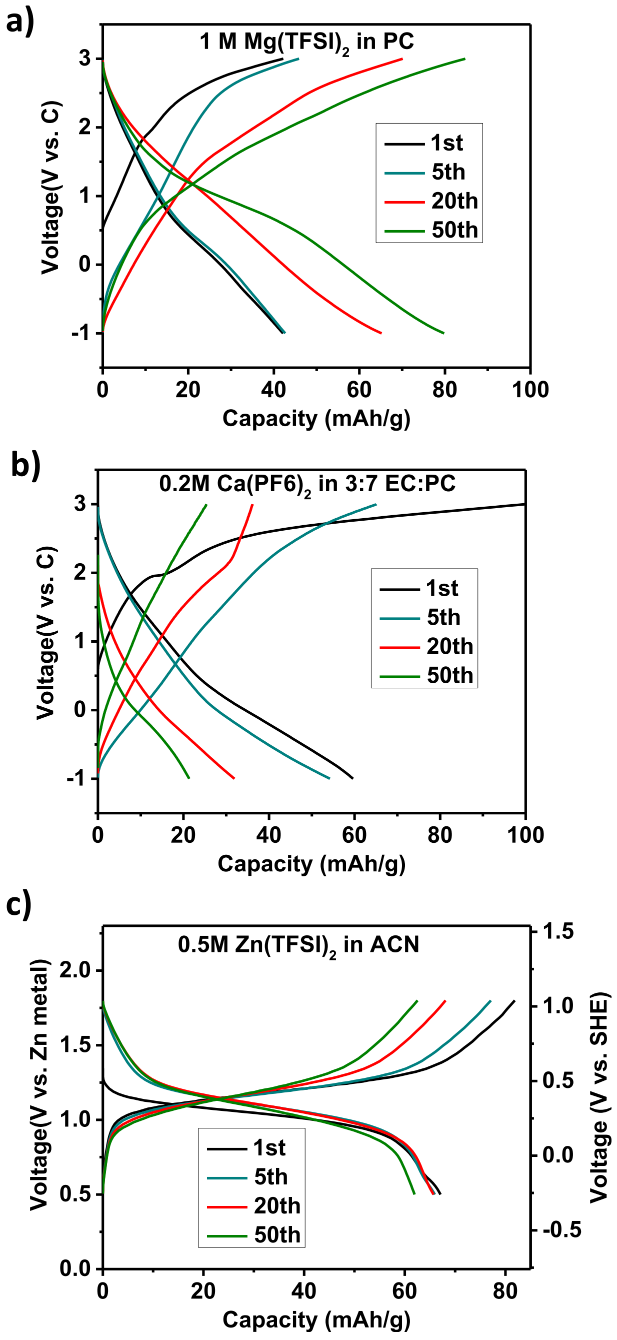

Fig. 1. Galvanostatic cycling (charging first, except for Zn) of multivalent ions at a rate of 10 mA g^{-1} with NFCN as the cathode. a) Using 1 M $Mg(TFSI)_2$ in PC as the electrolyte with a BP2000 carbon anode, b) using 0.2 M $Ca(PF_6)_2$ in 3:7 EC:PC with a BP2000 carbon anode, and c) using 0.5 M $Zn(TFSI)_2$ in ACN with a Zn metal anode.

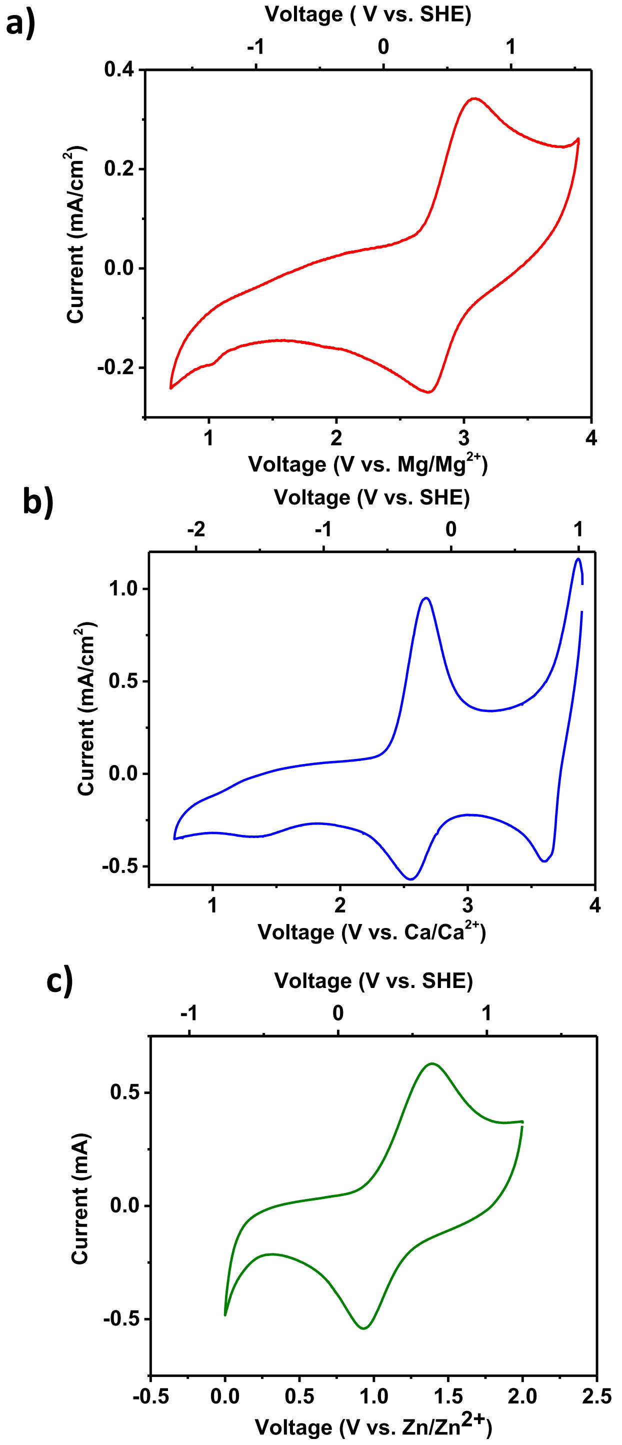

Fig. 2. Cyclic voltammograms for NFCN as the working electrode at a rate of 1 mV/s a) Using 1 M $Mg(TFSI)_2$ in PC as the electrolyte with a BP2000 carbon counter electrode and a Ca metal reference, b) using 0.2 M $Ca(PF6)_2$ in 3:7 EC:PC with a BP2000 carbon counter electrode and a Ca metal reference, and c) using 0.5 M $Zn(TFSI)_2$ in ACN with a Zn metal counter electrode and reference. Voltages for the Mg and Ca systems are converted to the standard potential using a ferrocene calibration.

including Mo_6S_8 (Chevrel) [3], V_2O_5 [5], λ-Mn_2O_4 [6], Prussian blue complexes [7–11], and many others [12,13]. Currently proposed Mg-ion intercalation cathodes typically exhibit low energy density, high overpotential, or they require high water content electrolytes to promote Mg insertion. For instance, Chevrel phase has a theoretical capacity of 129 mA h/g between 1 V and 1.3 V [3], which is less than one third of the voltage that is theoretically achievable in Li-ion systems. In the example of V_2O_5, only low intercalation capacity can be obtained unless substantial amounts of water are present in the electrolyte [14].

Prussian blue type complexes have been explored extensively for use in Na and Li based nonaqueous batteries [15–19], making them a promising candidate for use with multivalent ions. Prussian blue type complexes, such as barium hexacyanoferrate, copper hexacyanoferrate and nickel hexacyanoferrate (NFCN), have been shown to intercalate Ca, Mg and Zn, but only in high water content