Materials Chemistry and Physics 149-150 (2015) 601–606

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Copper hexacyanoferrate with a well-defined open framework as a positive electrode for aqueous zinc ion batteries

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HIGHLIGHTS

- A new material was investigated as anode materials for zinc ion battery.
- The material can be used in aqueous solution.
- The specific discharging capacity of 56 mA h g^{-1} is obtained at 20 mA g^{-1}.
- These results are helpful to develop new materials for rechargeable battery.

ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form
25 October 2014
Accepted 2 November 2014
Available online 12 November 2014

Keywords:
Inorganic compounds
Chemical synthesis
Electron microscopy
Electrochemical properties
X-ray photoemission spectroscopy

ABSTRACT

The feasibility of the electrochemical zinc ion insertion/extraction reaction in CuHCF nano-cube in aqueous solution is investigated. It is demonstrated for the first time that the divalent zinc ions can be reversibly inserted/extracted into/from CuHCF nano-cube in aqueous solution due to the small radius steric effect of zinc ions. The zinc ion insertion and extraction is controlled by the solid phase diffusion into/from the CuHCF electrode. Divalent cation (de)intercalation discovered in this work expands perspectives on intercalation electrochemistry of divalent cations, and it will possibly lead to development of novel divalent cation intercalation compounds for aqueous rechargeable batteries.

1. Introduction

In a world with a growing concern about energy management issues, energy storage devices are the most viable and efficient methods for storing the electricity generated from various intermittent and renewable sources, such as solar and wind energy [1]. An ideal energy-storage device that is characterized by high capacity, fast charge–discharge capability, safety, environmental friendliness, and low cost is of vital important for the development of the world [2,3]. Currently lithium ion batteries are considered as one of the most promising technologies due to their long lifetime and high energy density [4]. However, for large-scale applications, there is increasing concern about the cost, the limitation of lithium terrestrial reserves and the security. Therefore, great efforts have been made to explore new low-cost and reliable electrochemical energy storage technologies [5–12].

The utility of electrochemical intercalation of polyvalent cations, such as Mg^{2+}, Ca^{2+}, Zn^{2+}, Al^{3+} or Y^{3+} into a number of metal oxides or sulfides in an organic system has been extendedly investigated [5–12]. The fundamental research opens up the possibility of developing batteries with potential practical applications.

$KMFe(CN)_6$, Prussian blue analogues, have a cubic framework with Fe(III) and M(II) on alternate corners of a cube of corner-shared octahedral bridged by linear $(C\equiv N)^-$ anions (Fig. 1), the low-spin Fe(III) bond only with C atoms, the high-spin Fe(II) only with N atoms, and $C\equiv N$ bond opens the faces of the elementary cubes for inserted ions to move between half-filled body-center positions

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http://dx.doi.org/10.1016/j.matchemphys.2014.11.014

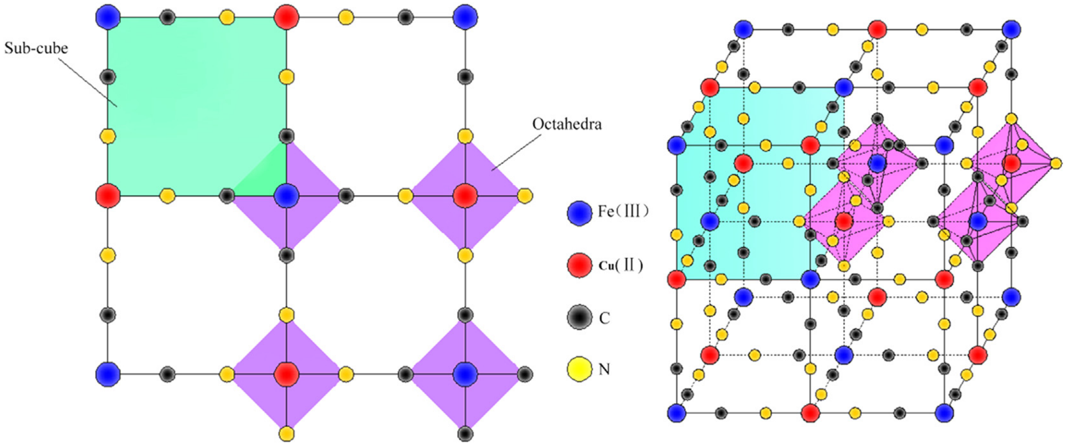

Fig. 1. Framework of Prussian blueanalogues.

[13–19]. Widman et al. [17] and later Wessells et al. [18,19] have investigated Na^+ and K^+ insertion into $KMFe(CN)_6$ (MHCF) with M = Cu and Ni. Their data invite exploration of reversible insertion of Na^+ into a Prussian blue analogue with an aqueous electrolyte [14–16]. It demonstrated that $KMFe(CN)_6$ could be a new framework of electrode materials for metal ion battery [13–16].

In this communication, the feasibility of the electrochemical zinc ion storage in copper hexacyanoferratenano-particles in $ZnSO_4$ ($Zn(NO_3)_2$ is the same) aqueous solution is firstly investigated for exploring aqueous zinc ion battery (ZIB).

2. Experimental

Co-precipitated CuHCF nano-powder was synthesized by simultaneously dropwise addition of 100 mL of 0.2 M $CuSO_4$ and 100 mL of 0.01 $K_3Fe(CN)_6$–50 mL H_2O during constant stirring. A tawny brown precipitate formed immediately. After sonicating for 30 min, the suspension was allowed to sit for eight hours. The precipitate was filtered, washed with water, and dried in air at 80 °C. The pH of the reaction system was controlled to be 7 ± 0.5 in the reaction time. The structure and composition of synthesized product was characterized by powder X-ray diffraction (XRD) obtained with a Philips X-ray diffratometer equipped with Cu Kα radiation ($\lambda = 1.5418$ Å). The angular resolution in 2θ scans was 0.02° over a 2θ range of 10–90°. The morphology of the materials was investigated using scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEM-2100, 200 kV).

To prepare electrodes, a mixture of 80% wt/wt CuHCF, 15% wt/wt acetylene black, 5% wt/wt polyvinylidene fluoride and some dimethylsulfoxide were ground by hand, creating homogeneous, black slurry. The slurry was spread on carbon plate current collectors with an area of 1 cm^2. The electrodes were dried in air at 80 °C.

Cyclic voltammetry measurements were carried out in a three-electrode set-up. The above prepared CuHCF electrode was used as the working electrode. The counter electrode was a graphite disk with a diameter of 2 cm and the reference electrode was a saturated calomel electrode (SCE). The electrolyte used in the experiment is 1 mol L^{-1} $ZnSO_4$ aqueous solution. In the three-electrode set-up, the graphite electrode is 2 cm apart from the working electrode. Galvanostatic electrochemical charge–discharge (C–D) analysis was carried out by a half cell under the potential window of 0–1.1 V vs SCE. To verify the feasibility of the zinc ion insertion, the surface state of the sample after the zinc ion insertion was further analyzed by X-Ray photoelectron spectroscopy (XPS, ESCALAB 250Xi (Thermo Fisher Scientific Inc.)).

3. Results and discussion

The XRD pattern in Fig. 2(a) shows that the synthesized CuHCF, which has the nominal formula $KCuFe(CN)_6$, forms a hexagonal lattice as has been reported [17]. As the XRD pattern obtained is in good agreement with the standard JCPDS pattern, the synthesized CuHCF is found to be phase-pure and its lattice parameter is 10.1 Å. As shown in the SEM and TEM images (Fig. 2(b–c)), the synthesized CuHCF consists of large agglomerations of nano-cubic particles with 50–100 nm side-length.

To evaluate the feasibility of the synthesized CuHCF nano-powder for ZIB application, electrochemical properties were examined by cyclic voltammetry analysis. Fig. 3(a) shows the cyclic voltammogram of the CuHCF cathode in aqueous $ZnSO_4$ electrolyte at a scanning rate of 1 mV s^{-1}. As the cyclic voltammogram obtained, a pair of cathodic and anodic peaks were observed for the zinc-ion battery with CuHCF nano-powder cathode under the potential window of 0.2–1.2 V. The pattern shown in Fig. 3(a) exhibited a cathodic peak at ~0.6 V and a corresponding anodic peak at ~0.8 V respectively, which may be attributed to the insertion/extraction of Zn^{2+} ions into and from the sub-cube of the face-centered cubic Prussian Blue crystal lattice structure of CuHCF nano-particle. The electrochemical reaction of CuHCF with Zn aqueous electrolyte can be expressed as [14–16],

$$xZn^{2+} + 2xe^- + CuHCF \Leftrightarrow Zn_xCuHCF \left(0 < x < 0.5\right) \quad (1)$$

To further evaluate the zinc ion insertion and extraction mechanism, CVs at different scanning rates are conducted, and the relationship between the peak current densities and scanning rate is investigated, which are presented in Fig. 3(b–d). It is well known that the relationship between the peak current density and potential scanning rate indicates two different electrochemical reaction characteristics, including solid-phase controlled or surface confined charge-transfer processes [12,20–22]. Here, the dependence of the cathodic and anodic peak current densities on the square root of the potential scanning rates confirms that the solid-phase diffusion process in the zinc ion insertion and extraction process is dominant for the reaction in the nano CuHCF electrode. According to the relationship as shown in equation (2):