



Reversible Calcium Ion Batteries Using a Dehydrated Prussian Blue Analogue Cathode



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ABSTRACT

Prussian blue analogue (KMFe-PBA), $K_xMFe(CN)_6 \cdot nH_2O$, was investigated as a new cathode material to insert/extract Ca^{2+} reversibly using a Ca-based organic electrolyte. A dehydrated KNiFe-PBA (i.e. $K_xNiFe(CN)_6$) electrode with a high electro-conductive additive demonstrated reversible capacities of ~ 50 mAh/g with Coulombic efficiencies of $\sim 92\%$ even though the decomposed capacity of the electrolyte was indicated at the discharge. During the 1st discharge and discharge-charge, a detailed structural characterization was performed using an ex-situ X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). XRD patterns and XPS spectra on the discharged and discharged-charged cathodes indicate that Ca^{2+} is inserted and extracted into and from the interstitial sites of KNiFe-PBA without destruction of the open framework structure.

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1. Introduction

During the last decade or two, lithium ion batteries (LIBs) have been commercially used for small electronic devices such as mobile phones and laptop computers due to their high energy density, rechargeability, and cycle-life [1,2]. In wider applications, LIBs installed in plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) have also been utilized in recent years by a few automotive companies [3]. However, further development of LIBs has been stymied with the limitation on their energy density, safety hazards, and deposits of lithium [4–9].

Recently, multivalent ion batteries (MIBs) have garnered significant attention with new rechargeable battery technologies as candidates for post-lithium ion batteries because of the higher energy density compared to that of LIBs [10–18]. The multivalent ions such as magnesium ions (Mg^{2+}), calcium ions (Ca^{2+}), and aluminum ions (Al^{3+}) are adapted to the working ions for MIBs in which divalent or trivalent ion can provide two or three electron redox couples, giving it a higher energy density in comparison with that of Li^+ [19]. Although some studies in MIBs with Mg^{2+} , Ca^{2+} or Al^{3+} have demonstrated its insertion and extraction in electrodes for LIBs, the performance of MIBs indicates that they are strongly affected by the characteristics of ions, electrodes, and electrolytes

[10–18]. As an example, Mg^{2+} , which possesses a similar radius to Li^+ [19], would evade the volumetric change of an electrode material during its insertion and/or extraction in the electrode. However, Mg^{2+} leads to a lower diffusion in the electrode than that of Li^+ because of the higher charge density on divalent ion with the similar radius to Li^+ .

One positive suggestion is calcium ion batteries (CIBs) due to their faster diffusion attributed to the lower charge density on its larger radius than that of Mg^{2+} [19], resulting in a higher reversible capacity. The additional advantages of calcium provide a lower reduction potential [20], a more abundant element [21] and a higher melting point [22] than those of magnesium. Thus, their characteristics suggest that CIBs possess a higher cell voltage corresponding to LIBs, a lower cost and greater thermal stability. Several materials for CIB electrodes have been experimentally and theoretically proposed as positive or negative electrodes which include vanadium oxides [14,15], manganese oxides [23,24] and topologically-defected graphenes [25]. Nonetheless, the larger ionic radius of Ca^{2+} compared to that of Mg^{2+} provides a limitation of its reversible insertion/extraction on their materials. For the reasons above, open framework materials with a large spacing in which multivalent ions can reversibly insert/extract have been investigated as MIB electrodes [16,26–29].

Prussian blue analogues (PBAs) have recently demonstrated the reversible insertion and extraction of mono- and multi-valent ions in both aqueous [16,30] and non-aqueous electrolytes [29] because of their large interstices which correspond to the A sites. In addition, the

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large A sites have been reported to accommodate large-sized ions and water molecules. The general formula of PBAs shows $A_xMM'(CN)_6 \cdot nH_2O$, where the A_x in the A sites is a guest ion or molecule such as Ca^{2+} , Mg^{2+} or H_2O , the M and M' are transition metal and the $-(CN)-$ is a chemical bond in the corner-shared octahedral (Fig. 1). The monovalent A_x ions coordinated in A sites vary from $x=0$ to 2 with corresponding the changing valence states of the M and M', suggesting that the electrochemical reaction of PBAs with the monovalent ion might be described by the following formula, $M^{(III)}M'^{(III)}(CN)_6 \cdot nH_2O + 2A^+ + 2e^- \rightleftharpoons A_2M^{(II)}M'^{(II)}(CN)_6 \cdot nH_2O$. However, the interstitial sites occupied by monovalent ions such as Na^+ were indicated to have structural distortions attributed to changes in the cyanide bonds of the cubic crystal structure with $Fm\bar{3}m$ space group (No. 225) to others, because excess Na^+ was inserted into the A sites with a charge compensation in the M, $M' = Mn$ frameworks [31]. Instead of the double monovalent ions in the A sites, a single divalent ion might offer promise in circumventing the structural evolution during two electron reaction. In addition, $A_xMFe(CN)_6 \cdot nH_2O$ ($M = Ni, Cu, Fe, Mn, Co,$ and Zn) was observed to be excellent rate and cycle performance due to the reversible conversion reaction [32].

As mentioned above, PBAs possess an attractive potential for consideration as compatible electrodes for MIBs, particularly CIBs which possess some advantages in cell voltage and costs. However, there are only a few researches reporting on PBA electrodes for CIBs in organic electrolytes which increase energy density and output voltage due to a wide potential window compared to that of aqueous electrolytes [16,29,30]. Here, we report on the electrochemical characteristics of $K_xMFe(CN)_6 \cdot nH_2O$ (KMFe-PBA) electrodes in organic electrolytes, changing systematically to the $M = Ni, Mn$ and Co , in addition to their structural characterization in the transition metal frameworks during Ca^{2+} insertion and extraction.

2. Experimental

2.1. Synthesis of KMFe-PBAs ($M = Ni, Mn$ and Co)

Prussian blue analogues (KMFe-PBAs) were synthesized by a wet chemical precipitation method. To substitute the M species in KMFe-PBAs for Ni, Mn, and Co, the precipitates were prepared as follows. $NiCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, and $CoCl_2 \cdot 6H_2O$ were separately dissolved in distilled water so as to correspond to 0.1 mol/L. The dropwise of the solution was then added with 1 mL/min into 50 mL of 0.5 mol/L $K_3Fe(CN)_6$ dissolved in distilled water at room temperature with constant stirring for 2 h. The 0.5 mol/L $K_3Fe(CN)_6$ for the Ni solution dropwise was only maintained at 80 °C [30]. The precipitated solution was repeatedly washed five times

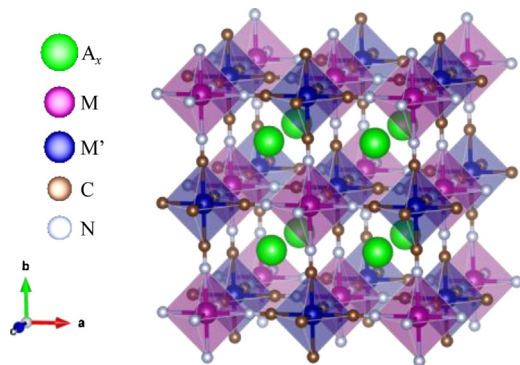


Fig. 1. Crystal structure of PBAs with the A_x represented in light green, the M and M' transition metal represented in violet and blue, the C and N presented in brown and silver at the corner-shared octahedral. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with distilled water by both centrifugation and ultrasonication to remove residues. The obtained precipitation was dried for 24 h under vacuum at 80 °C to reduce water content.

2.2. Structural characterization

To evaluate the crystallinity of the resultant samples, the powder X-ray diffraction (XRD) patterns were recorded at an angular range of 2θ from 10° to 90° by a Multiflex diffractometer (Rigaku, Japan) with Cu-K α source set at 40 kV and 40 mA. The macro-morphology was characterized by field emission scanning electron microscopy (FE-SEM, SU8000 Type II, Hitachi, Japan) with an energy dispersive X-ray spectroscopy (EDX, EMAX ENAGY EX-250, Horiba, Japan). Surface elemental analysis was carried out by an X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM-CI, Ulvac-Phi) using Al-K α line with an emission current of 2 mA and an accelerate voltage of 15 kV.

2.3. Electrochemical characterization

In order to confirm the original electrochemical performance of KMFe-PBA electrodes during the discharge (defined as insertion of ions) and charge (defined as extraction of ions), galvanostatic discharge and charge capacities were observed in a 2032 type coin cell using 1 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1 obtained from Kishida chemical corp. The composite positive electrodes were prepared by compressing a mixture of KMFe-PBA powder, carbon powder, and polytetrafluoroethylene (PTFE, Polyflon™ F-104, Daikin) at a weight ratio of 70:25:5. We attempted to improve electrical conductivity by employing two species of carbon powders with different specific surface areas, acetylene black (AB, Denkikagaku Kogyo) and ketjen black (KB, EC300J, Lion Corp.). As a counter electrode, lithium metal was adapted and separated from the KMFe-PBA electrode by a microporous polypropylene separator (Celgard® #3501). The cells were cycled galvanostatically at 25 $\mu A/cm^2$ in a voltage range from 2.5 to 4.3 V using a potentiostatic-galvanostatic system (TOSCAT-3100, Toyo System). In addition, the cells were maintained at 20 °C by a thermostatic bath (IN802, Yamato) during the charge-discharge cycles.

The electrochemical behaviors of Ca^{2+} into KMFe-PBA electrodes were investigated by galvanostatic charge/discharge curves and cyclic voltammograms (CVGs) using the potentio-galvanostat and an electrochemical analyzer (650A, ALS), respectively. All electrochemical measurements were conducted in standard three-electrode cells with KMFe-PBA electrodes as working electrodes made in the above conditions, Ag/Ag^+ electrodes as references, and porous electrodes as counter electrodes consisted of activated carbon (AP11-0010, ATEC), AB, and PTFE at a weight ratio of 80:10:10. The cells were cycled three times with a potential scan rate of 0.05 mV/s and a potential limit between -1.0 and 1.0 V vs. Ag/Ag^+ , and were discharged and charged twelve times at 25 $\mu A/cm^2$ in the same potential range. The electrolyte employed in all measurements was 0.5 mol/L calcium bis-trifluoromethylsulfonamide ($Ca(TFSI)_2$) dissolved in acetonitrile (AN).

3. Results and discussion

As shown in Fig. 2, the XRD patterns of the as-synthesized powder all exhibit main diffraction peaks corresponding to the peaks of the similar open framework structure (No. 46-0906) without the formation of other crystal structures, even though all peaks shift due to the differences in transition metal size and the amount of residues (K^+ and water molecules) in the structures [19,33]. In addition, atomic composition in KMFe-PBAs (Fig. 3(a–c))

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