EQCM Analysis of Redox Behavior of CuFe Prussian Blue Analog in Mg Battery Electrolytes

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Abstract: Rechargeable Mg batteries have received intensive attention as affordable rechargeable batteries with high electromotive force, high energy density, and high safety because of the following superb properties of Mg: Mg possesses two valence electrons and has the lowest electron affinity; Mg metal hardly forms dendrites; and Mg is a lightweight and so-called soluble or insoluble form. Electrochemical Society Active Member.

Keywords: Mg batteries; redox behavior; CuFe-PBA; EQCM; XAS

A wide variety of ions and molecules can be accommodated in the framework structure of Prussian blue (PB) and its analogs (PBAs). Mono- and polyvalent ions accommodated in the PB framework structure and PBAs can be extracted or re-inserted by redox reactions of transition metal ions composing the framework for charge compensation. In the present work, we report the detailed mechanism of the electrochemical insertion/extraction of Mg2+ ions and the effect of anions on the redox chemistry of a PBA composed of Cu and Fe ions by electrochemical quartz crystal microbalance and X-ray absorption spectroscopy. Furthermore, we evaluated the PBA as an active material using aqueous and organic electrolytes for Mg battery systems, and clarified that the redox potential of CuFe-PBA is approximately 3 V vs. Mg/Mg2+ in both aqueous and organic electrolytes.

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Experimental

Synthesis of a Prussian blue analog CuFe-PBA.— All chemicals for the synthesis of CuFe-PBA and electrochemical tests in aqueous electrolytes were reagent grade and used as received from the supplier (Nacalai Tesque, Inc., Japan) without additional purification. CuFe-PBA was synthesized as follows. An aqueous solution containing 20 mM CuCl2·2H2O (150 mL) was added dropwise to an aqueous solution containing 20 mM Fe(CN)6 3−·4H2O (150 mL) with stirring at more than 700 rpm. The resulting precipitates were separated by centrifugation. The separated precipitates were well washed by deionized water, followed by drying at 80 °C in air. The precise composition of CuFe-PBA was evaluated to be K1.6Cu[Fe(CN)6]0.9·1.4H2O by CHN analysis (Elementar Analysensysteme, GmbH, vario MICRO cube, Germany), inductively coupled plasma atomic emission spectroscopy (Seiko Instruments, Inc., SPS3000, Japan) for Cu and Fe elements, and atomic absorption spectrometry (Hitachi High-Technologies Co., Z-2300, Japan) for K element, suggesting that nearly all of iron ions in CuFe-PBA were reduced from the +II to +I oxidation state during synthesis.

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Figure 1. Structure of a PBA A2[M+][M’n(CN)n]·nH2O. Cations A and water are accommodated in A-sites. For CuFe-PBA, M and M’ are Fe and Cu ions, respectively. Defectiveness of this structure is neglected for simplicity, i.e. so-called soluble or insoluble form.
Characterization of CuFe-PBA.— All characterizations of CuFe-PBA were conducted at room temperature. Pt-sputtered circular 9 MHz AT-cut quartz crystal substrates with a diameter of 5.0 mm were used to measure the mass change by quartz crystal microbalance (QCM). Each composite positive electrode was prepared by coating the QCM substrate with a mixture of the PBA powder (active material), acetylene black (conductive agent), and Polyvinylidene difluoride (PVdF, binder) at a weight ratio of 8:1:1. The charged and discharged capacities were both about 40–45 mAh g⁻¹ during the potential sweep. During the first-cycle anodic sweep, in addition to the small redox peak couple at around 0.38 V, a large anodic peak is seen at approximately 0.98 V, which corresponds to the extraction of K⁺ ions originally accommodated in CuFe-PBA. After the 1st cycle, this large anodic peak splits into two peaks, while two cathodic peaks are seen at about 1.02 V and 0.80 V from the beginning. Therefore, three redox peak couples exist in the voltammogram after the first-cycle anodic sweep. However, possible electrochemically active redox couples are two pairs, i.e. FeIII/FeII and CuII/CuI,25,39 and it is impossible to specify the three redox peak couples only by the voltammograms. Figure 3b shows the mass change of the CuFe-PBA electrode at the 2nd cycle measured by electrochemical QCM and (c) fraction of Mg²⁺ ions as carrier ions calculated from the mass change under the assumption that completely dehydrated Mg²⁺ ions and SO₂⁻ ions are the carrier ions. Labels (i)–(v) show the points corresponding to the final potential of potentiostatic controls for the investigation on X-ray absorption fine structure described later.

Results and Discussion

Fig. 3a shows the cyclic voltammograms measured for CuFe-PBA. The charged and discharged capacities were both about 40–45 mAh g⁻¹ during the potential sweep. During the first-cycle anodic sweep, in addition to the small redox peak couple at around 0.38 V, a large anodic peak is seen at approximately 0.98 V, which corresponds to the extraction of K⁺ ions originally accommodated in CuFe-PBA. After the 1st cycle, this large anodic peak splits into two peaks, while two cathodic peaks are seen at about 1.02 V and 0.80 V from the beginning. Therefore, three redox peak couples exist in the voltammogram after the first-cycle anodic sweep. However, possible electrochemically active redox couples are two pairs, i.e. FeIII/FeII and CuII/CuI,25,39 and it is impossible to specify the three redox peak couples only by the voltammograms. Figure 3b shows the mass change of the CuFe-PBA electrode at the 2nd cycle measured by electrochemical QCM. It should be noted that Sauerbrey equation (Equation 1) is valid when the deposited film thickness is less than 0.15 μm.46 In the present study, the thickness of the composite electrode was about 20–30 μm as shown in Fig. 2. In addition, it has been reported that the deformation of the composite electrode significantly affects the frequency and dissipation changes.47,48 Thus, for more quantitative discussion, it is required to discuss the change in the resonance peak width (the imaginary component of the quartz crystal admittance) in addition to the resonance frequency shift (the real component of the quartz crystal admittance).48 By considering the fact above, it is possible that the calculated mass change shown in Fig. 3b is not quantitatively accurate.
Nevertheless, the direction of the mass change (mass increase or decrease) is correct, which assures the discussion below. The mass of CuFe-PBA decreases for the left two anodic peaks and increases for the right anodic peak during anodic sweep, while the mass of CuFe-PBA constantly increases during the cathodic sweep. The slope of the mass increase is slightly higher for the left cathodic peak than for the right. Focusing on the two redox peak couples at about 1.02 V and 0.80 V, the behavior of the left redox peak couple at 0.80 V is consistent with the expected mass change: the mass increases during cathodic reaction because Mg$^{2+}$ ions are inserted and compensate the charge, and the mass decreases during anodic reaction because of Mg$^{2+}$ and K$^+$ ions are extracted from the structure. In contrast, the mass change is opposite to expectations during the anodic sweep above 0.95 V vs. SHE, which implies that anionic species such as SO$_4^{2-}$ and OH$^-$ contribute to charge compensation. It is possible that these anionic species are inserted during anodic reaction and are extracted during cathodic reaction; the size of a SO$_4^{2-}$ ion is approximately 3.5 Å, which is smaller than the channel size of the CuFe-PBA framework (~5.0 Å). Conversely, as the diameter of the hydrated Mg$^{2+}$ ion is reported to be larger than 6 Å, partial or full dehydration is necessary for the insertion of Mg$^{2+}$ ions; the partial dehydrogenations of Mg$^{2+}$ and other cosmotropic ions have been also confirmed by EQCM during adsorption into carbon materials and a state-of-the-art multilayered 2D Ti$_3$C$_2$T$_x$ MXene, where Ti$_3$ stands for a general surface termination.

For a more quantitative discussion, the fraction of Mg$^{2+}$ ions as carrier ions was calculated from the mass change during the 2nd cycle by the following equation under the assumption that completely dehydrated Mg$^{2+}$ and SO$_4^{2-}$ ions are the carrier ions:

$$x(\%) = \frac{n_a M_a - n_c M_c F \Delta m / Q}{n_a M_a + n_c M_c} \times 100$$

where $x$ is the fraction of carrier cations, $F$ is the Faraday constant (96,485 C mol$^{-1}$), $\Delta m$ is the mass change measured by quartz crystal microbalance, $Q$ is the electrical charge flowed, $M_a$ and $M_c$ are the formula weights of anion and cation, and $n_a$ and $n_c$ are the valence numbers of the anion and cation, respectively. In the present work, completely dehydrated Mg$^{2+}$ ion and SO$_4^{2-}$ ion are considered to be the carrier anion and cation, respectively, i.e. $M_a = 95.86$ g mol$^{-1}$, $M_c = 24.31$ g mol$^{-1}$, $n_a = -2$, and $n_c = +2$. As shown in Fig. 3c, the fraction of Mg$^{2+}$ ions is approximately 85% below 0.9 V and approximately 75% above 0.9 V during the anodic sweep, indicating that the contribution of SO$_4^{2-}$ ions increases above 0.9 V. During the cathodic sweep, the fraction is nearly constant although a flexion point is seen at approximately 0.82 V. The contribution of anionic species was postulated by Itaya et al., and was experimentally verified by Malik et al. using the radiotracer method. Also in the present study, the contribution of anionic species was substantiated by EQCM measurement. It should be noted that the fraction of Mg$^{2+}$ ions would be smaller when considering hydrated or partially dehydrated Mg$^{2+}$ ions as carrier ions. In addition, proton can be a carrier ion although the concentration of the protons (about 10$^{-7}$ M) is much smaller than that of Mg$^{2+}$ ions (1 M). As described above, the fraction of Mg$^{2+}$ ion as a carrier ion is calculated to be approximately 85% below 0.9 V during the anodic sweep. Because the mass of Mg$^{2+}$ ion is about 24 times larger than proton, and thus, it is impossible to elucidate the mass change (i.e. the mass decrease under the oxidation reaction) by considering only proton as a carrier ion.

For the investigation on valence change of Cu and Fe, CuFe-PBA samples held at various potentials were examined by XAS. Fig. 4 shows the chronocoullograms under the various potentiostatic controls in the range of 0.7–1.2 V vs. SHE. Capacities are converted after each potentiostatic control for 1 h, suggesting that the potentiostatic control for 1 h is sufficient to obtain the steady valence states of Fe and Cu ions. Figure 5 shows the X-ray absorption spectra around Fe K-edge and Cu K-edge before and after the potentiostatic controls. As shown in Fig. 5, the position of the Fe K-edge is significantly sensitive to the holding potentials, and becomes more positive when the final holding potential is increased, irrespective of the intermediate potential controls. The position of Fe K-edge of these spectra is between those of the reference spectra of K$_3$Fe(CN)$_6$ and K$_2$Fe(CN)$_6$, indicating that an electrochemically active redox couple is Fe(II)/Fe(III). In contrast, the X-ray absorption spectra around the Cu K-edge is mostly unchanged including the valence-sensitive pre-edge peaks at about 8985 eV; the pre-edge peak corresponding to Cu(II) at 8986 eV remains after all the potentiostatic controls. Although a small pre-edge peak corresponding to Cu(I) at 8984 eV remains after all the potentiostatic controls. Thus, it can be concluded that the electrochemically active redox couple is Fe(II)/Fe(III), and that the peak splitting occurs as a result of changes in the carrier ion fraction above 0.7 V. Incidentally, the small redox peak couple below 0.6 V corresponds to the redox reaction of Cu(II)/Cu(I) by considering the fact that the redox couple Cu(II)/Cu(I) also contributes to the redox reaction.

Figure 4. Chronocoullograms measured in an aqueous electrolyte containing 1.0 M MgSO$_4$ (pH 6.8) under the potentiostatic controls of (a) 1.2 V, (b) 1.2 V→1.0 V, (c) 1.2 V→0.7 V, (d) 1.2 V→0.7 V→0.9 V, and (e) 1.2 V→0.7 V→1.2 V vs. SHE. Holding time for each potential is 1 h.
of CuFe-PBA.\textsuperscript{25,39} In contrast, as shown in Fig. 6, the redox peak couple is not seen below 0.6 V in a 0.5 M K$_2$SO$_4$ aqueous electrolyte, suggesting that the accompaniment of the redox reaction of Cu$^{II}$/Cu$^{I}$ is particular to the insertion of divalent Mg$^{2+}$ ions. Nevertheless, the predominant active redox couple is Fe$^{III}$/Fe$^{II}$ by comparing the magnitude of each peak current. It should be also noted that the CuFe-PBA containing Cu(II) ions at interstices (A sites) exhibits the obvious redox peak couple of Cu$^{II}$/Cu$^{I}$ in a K$_2$SO$_4$ electrolyte,\textsuperscript{25} but this possibility is excluded in the present case because the relative ratio of Cu to Fe is almost unity (K$_{1.6}$Cu[Fe(CN)$_6$]$_{0.9}$·1.4H$_2$O), and the Cu(II) ions are considered to exist as lattice ions (bridged to iron through -NC groups).

As described above, anionic species such as SO$_4^{2-}$ act as carrier ions in addition to Mg$^{2+}$ ions in 1.0 M MgSO$_4$ aqueous electrolyte. The emergence of the contribution of anionic species for charge compensation is possibly due to incomplete dehydration of Mg$^{2+}$ ions caused by the strong electrostatic constraint, which requires a larger volume to be inserted; the tight spacing in the CuFe-PBA framework structure can be alleviated by the inverse action of cations and anions for the charge compensation. In fact, monovalent K$^+$ ions with a larger ionic radius are reversibly inserted/extracted through an almost complete dehydration in PB without an obvious peak splitting in a KCl aqueous electrolyte.\textsuperscript{15,27} However, mixed charge compensation with cations and anions is also seen for CuFe-PBA in a K$_2$SO$_4$ aqueous electrolyte as shown in Fig. 6, although peak splitting is significantly suppressed. Therefore, the peak splitting and the mixed charge compensation depend on all of the following factors: the size and defectiveness of the framework structure (insoluble or soluble form\textsuperscript{15}), the number of valence electrons of carrier ions, and the sizes of solvated or desolvated carrier ions. It should be noted that peak splitting can also be caused by the mixture of PBAs with different stoichiometries, for example, K$_2$Co$^{II}$[Fe$^{II}$(CN)$_6$] and KCo$^{II}$[Fe$^{II}$(CN)$_6$] in a cobalt hexacyanoferrate system.\textsuperscript{18,22}

![Figure 5](image1.png)

**Figure 5.** X-ray absorption spectra around (a) Fe $K$-edge and (b) Cu $K$-edge for as-synthesized CuFe-PBA. (i) CuFe-PBA after the potentiostatic controls of 1.2 V, (ii) 1.2 V → 1.0 V, (iii) 1.2 V → 0.7 V, (iv) 1.2 V → 0.7 V → 0.9 V, and (v) 1.2 V → 0.7 V → 1.2 V vs. SHE. Holding time for each potential is 1 h.

![Figure 6](image2.png)

**Figure 6.** Cyclic voltammogram and corresponding mass change of CuFe-PBA electrode measured by electrochemical QCM in 0.5 M K$_2$SO$_4$ aqueous electrolyte at 1.0 mV s$^{-1}$.

![Figure 7](image3.png)

**Figure 7.** (a) Charge-discharge curves for CuFe-PBA measured in a 1.0 M MgSO$_4$ aqueous electrolyte with 1 C rate and (b) changes in charge and discharge capacities as a function of cycle. The cutoff potentials were set to 1.10 and 0.25 V vs. SHE.
Figure 8. Cyclic voltammogram and corresponding mass change of CuFe-PBA electrode measured by electrochemical QCM in 0.50 M Mg(TFSA)2 triglyme electrolyte at 1.0 mV s−1.

Figure 7 shows the charge-discharge curves and changes in capacities with cycles for CuFe-PBA measured in a 1.0 M MgSO4 aqueous electrolyte at 1 C rate. CuFe-PBA has a relatively high cycle capability and shows a discharge capacity above 42 mAh g−1 after 38 cycles. However, there is a gap of approximately 20 mAh g−1 between the charge and discharge capacities, which is because of oxidative decomposition of the water solvent; the equilibrium potential of the redox couple O2/H2O, E(O2/H2O) is 0.83 V vs. SHE at pH 6.8, and thermodynamically, oxidative decomposition can occur above 0.83 V. Furthermore, the redox potential of the Mg2+/Mg redox couple is also out of the potential window (stable potential region) of aqueous electrolytes, and Mg metal cannot be used for the negative electrode. Therefore, it is impossible to construct rocking chair-type Mg batteries using aqueous electrolytes, which is not favorable for practical applications.

Therefore, we also conducted an electrochemical test in triglyme electrolyte containing 0.50 M Mg(TFSA)2. Figure 8 shows the cyclic voltammogram and corresponding mass change of the CuFe-PBA electrode measured in the triglyme electrolyte. One redox peak couple is seen at around 3.1 V vs. Mg/Mg2+ and splitting is not seen in either peak. The small oxidation peak (bump) at about 3.6 V corresponds to the oxidative decomposition of the electrolyte. The intensity of the redox peak couple is smaller than those in 1.0 M MgSO4 aqueous solution, and the charged and discharged capacities were both about 2 mAh g−1 during the potential sweep. This result implies the slow insertion and extraction of Mg2+ ions, but not the fast adsorption and desorption of other ionic species, such as TFSA− ion; the maximum diameter of the TFSA− anion is approximately 7.4 Å and much larger than the framework size of CuFe-PBA. Although the mass change during the potential sweep apparently shows the adsorption of the oxidative decomposition product of the electrolyte above 3.6 V vs. Mg/Mg2+, the expected mass change, i.e. the increase in mass during cathodic reaction and decrease during anodic reaction, was not observed in the potential range of 2.3–3.6 V. However, the fraction of Mg2+ ions as carrier ions was calculated to be approximately 95% both in the anodic and cathodic sweeps using equation 2 under the assumption that completely desolvated Mg2+ ions and TFSA− ions are the carrier ions; the formula weight of TFSA− ion is 280.13 g mol−1, and even the adsorption/desorption of slight amount of TFSA− ions hinders the measurement of the mass change contributed by the insertion/extraction of Mg2+ ions. When Mg2+ ions mainly contribute to the charge compensation of CuFe-PBA, complete desolvation is necessary for the insertion of Mg2+ ions because the maximum length of triglyme is approximately 14.7 Å. The resulting bare Mg2+ ions strongly interact with the constituents of the CuFe-PBA framework, i.e. cyano groups and Cu and Fe ions, retarding Mg2+ ion diffusion; in turn, incomplete desolvation can be used to alleviate the strong electrostatic constraint of Mg2+ ions. These phenomena are summarized in Fig. 9. This fact can be a guideline for choosing solvents when using active materials with framework structures for polyvalent batteries where strong electrostatic constraints are forecasted.

Conclusions

We investigated the possibility for using CuFe-PBA as an active material for Mg batteries in detail by EQCM and XAS. Through this work, we have reached the following conclusions:

1. CuFe-PBA works as an active material for Mg batteries at room temperature. The capacity of CuFe-PBA is 40–60 mAh g−1 over 30 cycles at 1 C rate in an aqueous electrolyte, and the redox potential of CuFe-PBA is approximately 3 V vs. Mg/Mg2+ in both aqueous and organic electrolytes.

Figure 9. Schematic illustration of the insertion of Mg2+ ions into CuFe-PBA in (a) MgSO4 aqueous electrolyte and (b) Mg(TFSA)2 triglyme electrolyte.
2. The main redox active species is Fe\textsuperscript{III}/Fe\textsuperscript{II} in CuFe-PBA, although the Cu ion valence also slightly changes.

3. Not only Mg\textsuperscript{2+} ions, but also anions, contribute to the charge compensation during charge and discharge in aqueous electrolytes, resulting in redox peak splitting. The peak splitting is not necessarily a drawback, but can be avoided by selecting appropriate sizes of the framework structure, solvent, and solutes (carrier ions).

4. Incomplete desolvation alleviates the electrostatic interaction of Mg\textsuperscript{2+} ions with the framework constituents, resulting in fast diffusion of Mg\textsuperscript{2+} ions.

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