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The Effect of Electrolyte Type on the Li Ion Intercalation in Copper Hexacyanoferrate

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Copper hexacyanoferrate (CuHCF) is proved to be a potential cathode for potassium ion and sodium ion storage in aqueous system recently. However, its ability for lithium ion storage has not been well studied. Here, we synthesized CuHCF by a low-cost and scalable co-precipitation method, and its electrochemical behavior as the cathode for lithium ion storage was investigated both in aqueous and organic systems. The CuHCF electrode shows larger capacity and better rate capability in organic system compared with the performance in aqueous system. In addition, the capacity has 88% retention after 500 cycles. We further analyzed the strain generated during lithium ion intercalation by ex-situ X-ray diffraction (XRD) method in both types of electrolyte. The lattice of CuHCF shows shrinkage with ion intercalation in both systems. The measured strains are 0.70% and 0.83% in aqueous and organic system, respectively. The results indicate that the large open framework and small strain are the essential factors for the promising electrochemical performance.

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Lithium ion batteries (LIBs) are the dominant component in portable electronics and electric vehicles in our daily life.¹⁻⁴ Recently, the need for large-scale energy storage on the electric power, such as solar/wind power grid is growing rapidly.^{5,6} However, it still challenge to use LIBs in large-scale electric energy storage due to the stationary energy storage requires long-term operation, high power with high round-trip energy efficiency, more importantly, low cost.⁵⁻¹⁰

Coordination polymers are promising electrode materials for large-scale energy applications because of their covalent and nanoporous host framework, such as metal organic framework (MOF) and Prussian blue analogues (PBAs).¹¹⁻¹³ Especially, PBAs have wide channels between large A sites, allowing rapid insertion and extraction of various cations, such as monovalent ions: Li⁺, Na⁺, and K⁺,¹⁴⁻¹⁷ divalent cations: Mg²⁺, Ca²⁺, and Ba²⁺,^{18,19} and trivalent cations: Al³⁺ and Y³⁺.^{20,21} The general chemical formula of PBAs is A_xP_y[R(CN)₆]_z · nH₂O, where A is an alkaline ion and P and R are nitrogen-coordinated transition metal ion and carbon-coordinated transition metal ion, respectively. Therefore, PBAs have a huge family depends on the variation of P and R sites. Among them, A_xP_y[Fe(CN)₆]_z · nH₂O is most studied group when R is occupied by iron.²²⁻²⁴ Yi Cui et al. studied copper hexacyanoferrate (CuHCF) as a cathode for K ion storage in aqueous electrolyte.²⁵ It shows ultra-long cycle life, high power, high energy efficiency and low cost, indicating CuHCF is a promising cathode electrode for grid-scale energy storage application. However, there are seldom studies on the electrochemical properties of A_xP_y[Fe(CN)₆]_z · nH₂O for Li ion storage and the comparison of storage properties between aqueous and organic system.

In this study, we investigated the electrochemical properties of CuHCF for Li ion storage in both aqueous and organic systems. It is found that the Li ion intercalation is influenced by hydronium in aqueous system. While CuHCF electrode delivers higher capacity and rate capability in organic system due to less water content and humidity. The specific capacity is more than 99 mAh/g at 0.1 C with high Coulombic efficiency (> 99.22%) and the retention is 88% after 500 cycles at 10 C. The average operating voltage is 3.3 V versus Li metal. Moreover, we studied the structural evolution of CuHCF upon Li ion intercalation by ex-situ X-ray diffraction (XRD) method in both aqueous and organic electrolyte. The lattice parameters show shrinkage during Li ion intercalation in both electrolytes. The shrinkage ratios are 0.70% and 0.83% in aqueous and organic system, respectively. These indicated that small strain generated in CuHCF with Li ion intercalation. Therefore, the large open channel and small struc-

ture change in CuHCF are the main contributions to the good Li ion storage properties.

Experimental

General synthesis of copper hexacyanoferrate.—Copper hexacyanoferrate particles were synthesized by co-precipitation method with an easy and high scalable process. Typically, 60 ml of 40 mM Cu(NO₃)₂ (Stream Chemicals) and 60 ml of 20 mM K₃Fe(CN)₆ (Alfa Aesar) were prepared in deionized (DI) water, respectively. Then the two solutions were mixed dropwise in 30 ml DI water at 40°C with vigorous stirring. The dropping speed is about one drop per second. A precipitation with tan color was formed in the process and allowed aging for 24 h, then followed by washing with DI water and acetonitrile in sequence with centrifuge. The materials were dried in vacuum oven at 40°C overnight and grounded to fine powders for further process.

Preparation of copper hexacyanoferrate electrode.—The slurry for CuHCF cathode was prepared by mixing 80 wt% CuHCF, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP), subsequently, it was coated on aluminum foil as the cathode electrode. The electrochemical properties of CuHCF cathode were investigated in a coin cell by using Li metal as the anode. The electrolyte was 1 M LiPF₆ in a solution of ethylene carbonate and diethyl carbonate (1:1 vol:vol). The separator is Celgard 2325 (Celgard). The mass loading of each electrode is about 2 mg which is measured by weighing the mass of Al foil before and after loading CuHCF. The accuracy of the balance is 0.002 mg (Mettler Toledo, XP26).

Morphology, composition and electrochemical characterization.—The morphologies of CuHCF were characterized by SEM (JEOL FESEM 7600F) and TEM (200 kV, JEOL 2010 UHR). The compositions were analyzed by XRD (Bruker D8 Advance Powder) and the lattice parameters were refined by the Le Bail fitting method. The elemental and chemical state in CuHCF were studied by XPS (Kratos AXIS Supra). The electrochemical tests were performed on a potential station (VMP 300, BioLogic). For the aqueous cell, it is performed in a flooded beaker cell with three electrode system, in which CuHCF as the working electrode, activated charcoal as the counter electrode and Ag/AgCl in 4 M KCl as the reference electrode. A coin cell with Li metal as the anode is assembled for studying in the organic electrolyte.

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Figure 1. Morphology and composition of CuHCF. (a) SEM image of CuHCF. (b) TEM image of CuHCF, it has a cubic shape with the size of ~ 100 nm. (c) The cubic structure of CuHCF, the large site in the structure can be occupied by various cations, such as Li ion. (d) X-ray diffraction patterns of CuHCF. The XRD data was fitted by the Le Bail fitting method in GSAS program. The red curve is the fitting data and the blue curve is the difference. (e) The scheme of Li ion intercalation in CuHCF in aqueous and organic electrolytes.

Results and Discussion

The morphology and composition of CuHCF was characterized in Figure 1. As shown in Figure 1a, the as synthesized CuHCF are nanoparticles and has a uniform distribution. TEM image in Figure 1b clearly exhibits its cubic shape with size around 100 nm. This is because of the natural cubic crystal structure of PBA as depicted in Figure 1c. The sharp cubic in Figure 1b also indicated the high crystallinity of CuHCF which is further confirmed by the XRD pattern in Figure 1d. All the diffraction peaks can be indexed well with the face-centered cubic $Fm-3m$ space group as previous studies.^{25,26} The calculated lattice parameter is $a=b=c=10.068$ Å by Le Bail fitting method in GSAS program. Figure 1e shows the scheme of Li ion intercalation with CuHCF in different electrolytes. The left side is in aqueous electrolyte, and in which Li ion is in hydration state. While the right one is in organic electrolyte, and in which Li ion is wrapped by larger EC, DEC molecules. This indicates that Li ion will undergo different processes when intercalated with CuHCF

and may deliver different electrochemical properties in these two systems.

Figure 2 shows the cyclic voltammetry (CV) at scan rate of 1 mV/s and charge-discharge curves at various rates both in aqueous and organic systems. Figure 2a is the CV curve of CuHCF in 1M LiCl aqueous solution with the scan rate of 1 mV/s. CuHCF has a very broad reaction range with Li ion in aqueous electrolyte and the initial cycle is consistency with the subsequent cycles. This may attribute to the hydronium also takes reaction with CuHCF in aqueous system.^{15,27,28} It was further proved by more CV studies in Figure 2b. The CV curves split to two clear redox peaks when the pH was adjusted to 2.8 at 1 mV/s. The reaction peak at 0.53 V vs. SHE is attributed to the reaction with lithium and the peak at 0.84 V vs. SHE comes from the hydronium. The hydronium peak becomes dominant when the scan rate reduced to 0.1 mV/s at pH 2.8. We further tested CuHCF electrode by CV scans in Na ion and K ion electrolytes which radius are larger than Li ion. Meanwhile, we controlled pH in both electrolytes. In Figure S1a, it shows one broad redox peak in 1 M NaNO₃

Figure 2. Electrochemical properties CuHCFE versus Li ion. (a) The cyclic voltammogram (CV) of CuHCFE in 1 M LiCl aqueous solution. (b) The CV comparison with different scan rate and different pH in 1 M LiCl electrolyte. (c) The CV of CuHCFE in 1M LiPF₆ EC, DEC (1:1) solution, the scan rate is 0.1 mV/s. (d) The galvanostatic cycling at 1C in aqueous system. (e) The galvanostatic cycling at various current densities, 0.1C, 0.2C, 0.5C, 1C, 2C, and 5C, respectively, using lithium metal as the anode in the organic system.

electrolyte at pH 1.70, 1.09 and 0.51, respectively. In addition, CuHCFE also shows one clear redox peak in K ion electrolyte at pH 1.82, 0.98 and 0.56, respectively (Figure S1b). Therefore, the intercalation of K ion and Na ion are not affected by hydronium, while the intercalation of Li ion is influenced by hydronium because of its lower reaction potential range. By contrast, the clear reduction and oxidation peaks are located at 3.06 V and 3.33 V versus Li/Li⁺ at the first cycle, respectively in organic electrolyte as shown in Figure 2c. They are shifted to 3.16 V and 3.34 V versus Li/Li⁺ at the subsequent cycles. The difference of the voltage at first cycles is attributed to the formation of solid electrolyte interface (SEI) at the initial cycle in the organic system. In addition, these cycles overlapped indicating the highly reversibility of the Li ion insertion.

Figure 2d shows the charge-discharge curves at 1C in 1 M LiCl aqueous electrolyte. The discharge capacity is 54 mAh/g with the sloping curve. Comparably, the reaction plateaus are much clear and flat at various current rates in organic system as depicted in Figure 2e. The observed capacities are 99, 89, 75, 66, 57, and 46 mAh/g at 0.1, 0.2, 0.5, 1, 2 and 5C, respectively. The capacities are larger than those in aqueous system because of the less water content and less humidity in organic system. The large capacity at low rate may be caused by the reduction of Cu²⁺ to Cu⁺ in addition to the reaction of [Fe(CN)₆]³⁻ → [Fe(CN)₆]⁴⁻.¹⁴ The discharge plateau is at 3.30 V versus Li/Li⁺ at 1 C. Moreover, the voltage hysteresis is small even at high rate of 5 C indicating high rate performance and long cycle life which are the crucial parameters for grid-scale storage.

The rate capability and cycling stability of CuHCFE in organic system are further studied and shown in Figure 3. The initial discharge capacity is 99 mAh/g with the CE of 78.33% and subsequently increased to more than 99.34% in the following cycles. The specific capacity has 91% retention even after high rate test at 15 C. The cycling stability test is shown in Figure 3b. The capacities are consistent with the values in Figure 3a. The specific capacity is 43 mAh/g at 10 C as shown in Figure 3b, it shows more than 88% capacity retention after 500 cycles. The CE is higher than 99.22% during the cycling (the blue

curve in Figure 3b). Therefore, CuHCFE electrodes show good and stable lithium ion storage properties.

We conducted XPS to study the evolution of valence state of metal ions in CuHCFE. Figure 4a is the survey spectra of as synthesized CuHCFE powder, CuHCFE electrode reduced by cyclic voltammetry scan at 0.1 mV/s (CuHCFE-CV), CuHCFE electrode reduced by galvanostatic cycling with potential limitation at 0.1 C (CuHCFE-GCPL), respectively. All the spectra show the distinguishing peaks of Fe, Cu, C, N and K. Meanwhile, Li and F are detected in CuHCFE-CV and

Figure 3. The rate capability and cycling stability of CuHCFE versus Li ion. (a) The rate capability of CuHCFE at various C rate with high coulombic efficiency of 99%. (b) The long-term cycling of CuHCFE at a 10 C rate.

Figure 4. The XPS data of as synthesized CuHCF and the reduced CuHCF by CV and GCPL method. (a) the XPS survey scan of CuHCF-powder, CuHCF-CV and CuHCF-GCPL, respectively; (b,c) the fine scan of Fe and Cu in CuHCF-powder; (d,e) the fine scan of Fe and Cu in CuHCF-CV electrode; (f,g) the fine scan of Fe and Cu in CuHCF-GCPL electrode.

Figure 5. The ex-situ XRD study of CuHCFE at different Li ion intercalation state in aqueous and organic electrolytes. (a-c) in aqueous electrolyte (d-f) in organic electrolyte. (a,d) The ex-situ XRD patterns of CuHCFE on Al foil/ carbon cloth with different state of Li ion interaction, 0% SOD means fully charged state, 100% SOD means fully discharged state. (b,e) The zoom-in of (400) peaks at different SOD. A clear shift of peaks to large diffraction angle is observed in both systems. (c,f) The lattice parameter change with the state of SOD, it shows both shrink tendencies upon Li ion intercalation.

CuHCFE-GCPL samples due to the intercalation of Li ion and un-removed solid electrolyte interface. We further investigated the evolution of Cu 2p and Fe 2p in these samples. All the fine scans were fitted after the C correction. As shown in Figure 4b, the Fe 2p in CuHCFE powder can be fitted with pairs of peaks, the peaks centered at 708.3 eV / 721 eV are from $\text{Fe}^{\text{II}}2p\ 3/2$ and $\text{Fe}^{\text{II}}1/2$, while the main peaks centered at 709.9 eV / 723.4 eV and 711.5 eV / 724.1 eV are assigned to $\text{Fe}^{\text{III}}2p\ 3/2$ and $\text{Fe}^{\text{III}}1/2$. Compared with Fe in CuHCFE powder, the Fe was fully reduced to Fe^{II} in CuHCFE-CV sample, as shown in the fine scan in Figure 2d. The peaks at 708.2 eV / 721.1 eV are from Fe^{II} . For Cu, in CuHCFE powder sample shows strong Cu^{II} satellite peaks at 943.61 eV / 963.24 eV. The Cu $2p_{3/2}$ peak can be fitted to 932.84 eV and 935.56 eV, which are assigned to Cu^{II} and Cu coordinated with N (Figure 4c).²⁹⁻³¹ In comparison, the peaks centered at 932.59 eV / 952.56 eV are mainly from Cu^{I} in CuHCFE-CV, no satellite peak of Cu^{II} is found. In CuHCFE-GCPL, the Fe^{III} is also fully reduced to Fe^{II} as shown in Figure 4f and Cu^{II} is partially reduced to Cu^{I} . Therefore, the increase of capacity in organic systems come from the partially reduced Cu ion.

Here, we also studied the lattice parameter change of CuHCFE at different state of discharge (SOD) in both aqueous and organic electrolytes by ex-situ XRD method (Figure 5). The CuHCFE electrodes were discharged to 0%, 20%, 40%, 60%, 80% and 100% SOD at 1 C, respectively. It is assumed that 0% SOD is the totally charged state indicating all Li ions are deintercalated from CuHCFE, and 100% SOD is the fully discharged state indicating Li ion are fully intercalated. For the samples in the aqueous system, they are discharged in the flooded beaker cell to the certain SOD, and washed with DI water for several times, then dried overnight in the vacuum oven. For the samples in the organic system, the coin cells were disassembled carefully and rinsed by dimethyl carbonate (DEC) three times in the glove box. The XRD data were collected by Bruker D8 Advance Powder. We used the same standard LaB_6 to do calibration before measuring our aqueous and organic samples. The calibration spectra can be checked in Figure S2.

The spectra and lattice parameter change curve were studied in Figure 5, (a-c) are in aqueous system and (d-f) are in organic system.

Both diffraction peaks of CuHCFE shifted to larger diffraction angles with the increased of state of SOD in these two systems (Figures 5a and 5d) which can be clearly detected from the zoom in peaks of (400) in Figures 5b and 5e. In addition, in Figure 5d, the peaks at 2θ of 65° and 78° are attributed to the diffraction of Al substrate, which maintain at the same positions with change of SOD.

The lattice parameters are calculated by the same Le Bail fitting method (Table I and Table II). It is worth to point out that the lattice parameter at 0% SOD is smaller in organic system, maybe due to the strain induced by the SEI layer during electrochemical process. The lattice parameters decreased with the Li ion intercalation in both systems indicating the lattice shrinkage. The shrink ratios are 0.70% and 0.83% in aqueous and organic electrolyte, respectively. Similar phenomenon is also observed in other PBAs aqueous systems.^{25,26} It is attributed to the decrease of radius of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ during the reduction of CuHCFE by Li ion.^{32,33} As for the difference on the shrink ratios, it may be because the difference solvation status in these two systems. Lithium ions are still in partially hydrated state by the water molecules which cause less bonding strength with ferrocyanide groups. While Li ion should be totally desolvated in organic system due to the large organic molecules, the bonding strength is larger than that in aqueous electrolyte corresponding to larger shrink ratio. In

Table I. The Le Bail method fitted XRD results for CuHCFE with Li ion intercalation in aqueous electrolyte. R_p is the reliable factor of profile, wRp is the weighted R factor of profile.

Material	$a=b=c$ (Å)	wRp (%)	R_p (%)
CuHCFE -0% SOD	10.12569(67)	3.00	2.20
CuHCFE-20% SOD	10.11687(69)	2.89	2.11
CuHCFE -40% SOD	10.09707(99)	3.65	2.30
CuHCFE -60% SOD	10.07951(91)	3.51	2.38
CuHCFE -80% SOD	10.05817(76)	3.28	2.26
CuHCFE -100% SOD	10.05461(85)	3.38	2.27

Table II. The Le Bail method fitted XRD results for CuHCFE with Li ion intercalation in organic electrolyte. Rp is the reliable factor of profile, wRp is the weighted R factor of profile.

Material	$a=b=c$ (Å)	wRp (%)	Rp (%)
CuHCFE -0% SOD	10.09394(106)	4.41	2.79
CuHCFE -20% SOD	10.08672(103)	4.35	2.72
CuHCFE -40% SOD	10.05598(100)	4.32	2.85
CuHCFE -60% SOD	10.03704(95)	4.57	2.84
CuHCFE -80% SOD	10.01978(99)	4.74	2.96
CuHCFE -100% SOD	10.00967(105)	4.58	2.79

comparison, the traditional cathode materials show larger lattice expansion during intercalation of Li ions, such as lithium cobalt oxide (LiCoO₂, 9.4%) and lithium manganese oxide (LiMnO₂, 8.2%).^{34–36} Based on these results, it can conclude that the high rate and cycling stability of CuHCFE cathode are attributed to the large open framework of CuHCFE and small lattice change during cycling.

Conclusions

In summary, we studied the CuHCFE as the cathode material for lithium ion battery in both aqueous and organic system. The electrode shows better rate capability and cycling stability in organic system. It is proved that the sloping reaction plateaus in aqueous electrolyte are from the reaction with hydronium. The specific capacity maintains 88% after 500 cycles at 10 C which is attributed to the high CE of >99.22% in organic electrolyte. Moreover, we investigated structural change upon Li ion intercalation by ex-situ XRD. The lattices show shrinkage in both aqueous and organic system. The shrink ratios are 0.70% and 0.83%, respectively. Therefore, the large open-framework as well as the small strain during Li ion intercalation indicates that CuHCFE is a promising cathode material for large-scale energy storage. In addition, the low-cost and scalable co-precipitation synthesis process will make CuHCFE an attractive candidate for large-scale stationary energy storage.

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