A concentrated electrolyte for zinc hexacyanoferrate electrodes in aqueous rechargeable zinc-ion batteries

D Kim, C Lee and S Jeong*
Department of Chemical Engineering, Soonchunhyang University, Asan, Chungnam 336-745, Republic of Korea
*E-mail: hamin611@sch.ac.kr

Abstract. In this study, a concentrated electrolyte was applied in an aqueous rechargeable zinc-ion battery system with a zinc hexacyanoferrate (ZnHCF) electrode to improve the electrochemical performance by changing the hydration number of the zinc ions. To optimize the active material, ZnHCF was synthesized using aqueous solutions of zinc nitrate with three different concentrations. The synthesized materials exhibited some differences in structure, crystallinity, and particle size, as observed by X-ray diffraction and scanning electron microscopy. Subsequently, these well-structured materials were applied in electrochemical tests. A more than two-fold improvement in the charge/discharge capacities was observed when the concentrated electrolyte was used instead of the dilute electrolyte. Additionally, the cycling performance observed in the concentrated electrolyte was superior to that in the dilute electrolyte. This improvement in the electrochemical performance may result from a decrease in the hydration number of the zinc ions in the concentrated electrolyte.

1. Introduction
In the area of energy storage research, aqueous rechargeable metal-ion batteries have attracted interest as possible substitutes for commercial aqueous batteries, such as lead-acid, Ni-Cd, and Ni-MH, because of their safety, low cost, high ionic conductivity, and environmental friendliness [1–8]. Among the various available systems, aqueous rechargeable zinc-ion batteries (ARZIBs) based on electrochemical insertion/extraction reactions of zinc ions have been widely studied and developed because of their advantages, including nontoxicity and safety [9–12]. These characteristics have been demonstrated by the wide application of ARZIBs to devices used in the body, such as hearing aids. In addition, ARZIBs are expected to have relatively high capacities because of the high theoretical value for zinc metal anodes (820 mAh g⁻¹), as well as low costs owing to their relatively simple manufacturing processes and the abundance of zinc resources [13–15].
In recent years, various materials, such as manganese dioxide and Prussian blue analogues (PBA), have been reported as cathode materials for ARZIBs [16, 17]. In particular, PBAs are notable potential cathode materials for application in ARZIBs owing to their superior characteristics, such as structural stability, large channels, and ease of synthesis [9, 18]. Additionally, these materials have large open sites (4.6 Å in diameter) and <100> channels (3.2 Å in diameter), which enable the rapid diffusion of various hydrated metal ions, including zinc ions [19–21]. However, the electrochemical performance of these materials has to be improved, as they exhibit relatively low capacities and capacity reduction during the initial cycles.
In this work, we applied a concentrated electrolyte in ARZIBs with PBA electrodes to improve the electrochemical performance by changing the hydration number of zinc ions. Our previous study demonstrated that the electrochemical performance of aqueous rechargeable calcium-ion batteries
could be improved by applying a superconcentrated electrolyte, and the improved performance was attributed to a decrease of the hydration number and radius of calcium ions [22]. Therefore, it was expected that the hydration number and radius of zinc ions could be changed by applying a concentrated electrolyte in ARZIB systems, which, in turn, would positively influence the electrochemical performance.

2. Experimental

Zinc hexacyanoferrate (Zn$_3$[Fe(CN)$_6$]$_2$, ZnHCF) powder, which is a PBA, was used as the active material. The synthesis process follows the method reported by Wang et al. [15]. However, as we wanted to further explore the ZnHCF synthesis method to optimize the cathode material for ARZIBs, in this study, three materials were synthesized by using aqueous solutions with three different concentrations of Zn(NO$_3$)$_2$ (Alfa Aesar, 99%). In brief, the materials were synthesized by simultaneously adding 120 mL of 0.05, 0.1, or 0.3 mol dm$^{-3}$ Zn(NO$_3$)$_2$ and 120 mL of 0.05 mol dm$^{-3}$ K$_3$Fe(CN)$_6$ (Sigma Aldrich, 99%) in a dropwise manner to 60 mL of deionized water under constant stirring at 80 °C. After sonicating for 30 min at 80 °C, the suspensions were aged for 6 h at 80 °C. Then, the precipitates were filtered and dried under vacuum at 30 °C for 24 h.

The structures and morphologies of the ZnHCF powders were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The XRD patterns were collected using two different devices. The ZnHCF powders synthesized using 0.1 and 0.3 mol dm$^{-3}$ Zn(NO$_3$)$_2$ were analyzed using a D8 ADVANCE diffractometer (Bruker AXS, Germany), whereas the powder synthesized using 0.05 mol dm$^{-3}$ Zn(NO$_3$)$_2$ was analyzed using a D/Max-2200PC diffractometer (Rigaku, Japan) equipped with a Cu Kα source (40 kV, 40 mA). The SEM images were collected using a SNE-3000M microscope (SEC, South Korea).

Charge/discharge and cycling performance tests were performed using a three-electrode cell with a ZnHCF electrode as the working electrode. A saturated calomel electrode (SCE) and activated charcoal were used as the reference and counter electrodes, respectively. The ZnHCF electrodes were prepared by casting a slurry including the ZnHCF active material powder (80 wt%), super P (9 wt%), graphite powder (2 wt%), and polyvinylidene fluoride (PVDF) as a binder (9 wt%, Sigma Aldrich) onto a carbon cloth (Fuel Cell Earth, USA) as a current collector. The coated electrode was dried under vacuum at 80 °C for 12 h. Prior to the electrochemical tests, the ZnHCF electrode was discharged from an open circuit voltage to 1 V in deionized water over 12 h to extract potassium ions. Then, the electrode was rinsed with deionized water and dried at 60 °C for 12 h. The dilute and concentrated electrolytes consisted of 1 and 3 mol dm$^{-3}$ Zn(NO$_3$)$_2$ dissolved in water, respectively. The electrochemical tests were performed on a WBCS3000 battery test system (WonATech, South Korea).

3. Results and discussion

First, to analyze the structure of the three synthesized materials, XRD patterns were collected. As shown in Fig. 1a and 1b, the peaks corresponding to the materials synthesized using 0.05 and 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$, respectively, are well-indexed to Zn$_3$[Fe(CN)$_6$]$_2$ (JCPDS 38-0688). However, as shown in Fig. 1c, different peaks are observed for the material synthesized using 0.3 mol dm$^{-3}$ Zn(NO$_3$)$_2$, which means that this material does not have a structure that is consistent with Zn$_3$[Fe(CN)$_6$]$_2$. Therefore, only the materials synthesized using 0.05 and 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ were used in the subsequent analyses and tests. Notably, the peaks in Fig. 1a are broader than those in Fig. 1b, which indicates that the material synthesized using 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ has superior crystallinity to that synthesized using 0.05 mol dm$^{-3}$ Zn(NO$_3$)$_2$. 


Figure 2 shows SEM images of the two materials synthesized using 0.05 and 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ dissolved in water. A comparison of Fig. 2a and 2b shows evenly distributed particles with relatively uniform sizes in the material synthesized using 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$, whereas particles with nonuniform sizes were observed in the material synthesized using 0.05 mol dm$^{-3}$ Zn(NO$_3$)$_2$. Thus, the materials synthesized using 0.05 and 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ dissolved in water showed differences in crystallinity and the degree of particle size uniformity.

To confirm differences in electrochemical performance between dilute and concentrated electrolytes, charge/discharge tests were performed using two different electrodes. Figures 3 and 4 show the charge/discharge curves of the ZnHCF electrodes synthesized using 0.05 and 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ dissolved in water, respectively, when the dilute and concentrated electrolytes were used. First, a comparison of Figs. 3 and 4 show that better electrochemical performance was exhibited by the ZnHCF electrode obtained from 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ than by that obtained from 0.05 mol dm$^{-3}$ Zn(NO$_3$)$_2$. In our previous study, it was demonstrated that a PBA electrode with a collapsed crystalline structure realizes relatively poor electrochemical performances in an aqueous electrolyte [22]. As indicated by the XRD results, the crystallinity of ZnHCF synthesized using 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ is to that of ZnHCF synthesized using 0.05 mol dm$^{-3}$ Zn(NO$_3$)$_2$, which likely accounts for the differences in the charge/discharge properties of the two ZnHCF electrodes.
On the other hand, in the charge/discharge curves, the electrochemical performance is notable improved in the concentrated electrolyte. As shown in Figs. 3 and 4, improved charge/discharge capacities are achieved in the concentrated electrolyte relative to those in the dilute electrolyte. In particular, as shown in Fig. 4 for the electrode obtained from 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$, the reversible charge/discharge capacity in the concentrated electrolyte is more than twice that in the dilute electrolyte. This increased capacity may result from the zinc ions having a decreased hydration number in the concentrated electrolyte. In the 1 and 3 mol dm$^{-3}$ Zn(NO$_3$)$_2$ electrolytes, the molar ratios of zinc ions to water molecules is 1:50 and 1:13, respectively. It has been reported that a zinc ion can have a hydration number of up to six in the first shell. If the secondary shell is included, the hydration number of a zinc ion increases to 18 [23, 24]. Additionally, the hydration number of a nitrate anion is known to be 3.7 [25]. Therefore, zinc ions in the concentrated electrolyte may have a smaller hydration number because there are insufficient water molecules in the concentrated electrolyte, whereas zinc ions in the dilute electrolyte can have the maximum hydration number. Zinc ions with a smaller hydration number can be inserted into and extracted from the ZnHCF electrode to a greater degree, which leads to increased charge/discharge capacities in the concentrated electrolyte.

**Figure 3.** Charge/discharge curves at 0.1 C of the ZnHCF electrode synthesized using 0.05 mol dm$^{-3}$ Zn(NO$_3$)$_2$ in (a) 1 and (b) 3 mol dm$^{-3}$ Zn(NO$_3$)$_2$.

**Figure 4.** Charge/discharge curves at 0.1 C of the ZnHCF electrode synthesized using 0.1 mol dm$^{-3}$ Zn(NO$_3$)$_2$ in (a) 1 and (b) 3 mol dm$^{-3}$ Zn(NO$_3$)$_2$. 
Improved electrochemical performance was observed not only in terms of charge/discharge capacities, but also in cycling performance. Cycling tests were carried out for the ZnHCF electrode synthesized using 0.1 mol dm\(^{-3}\) Zn(NO\(_3\))\(_2\) dissolved in water owing to the better charge/discharge capacities of this electrode. Figure 5 shows the cycling performance over 150 cycles at 5 C in both dilute and concentrated electrolytes. The capacity gradually increased during the initial cycles in both electrolytes. The reason for this phenomenon is unclear at present and a detailed interpretation is beyond the scope of this work, but it may be related to activation or conditioning effects [20, 21, 26].

As shown in Figs. 5a and 5b, improved cycling performance is observed in the concentrated electrolyte. In our previous study, it was demonstrated that the crystalline lattice structure of an electrode could be maintained after cycling if the hydration number of the cations were decreased, leading to improved cycling performance [22]. Therefore, in this study, the reason for the improved cycling performance in the concentrated electrolyte may be the decreased hydration number of the zinc ions. The ZnHCF electrode may experience structural stress owing to repeated insertion/extraction of hydrated zinc ions with a larger hydration number and radius during cycling in the dilute electrolyte, resulting in capacity reduction. However, this phenomenon might be suppressed in the concentrated electrolyte because the zinc ions have a relatively smaller hydration number and radius, resulting in improved cycling performance.

4. Conclusions
We applied a concentrated electrolyte to improve the electrochemical performance in an ARZIB system. In charge/discharge tests, improved charge/discharge capacities were observed in the concentrated electrolyte, which may be attributed to a small hydration number and radius of zinc ions. Additionally, the cycling performance was also improved in the concentrated electrolyte, probably because the structural stress experience by the ZnHCF electrode was suppressed in the concentrated electrolyte during cycling owing to the decrease in the hydration number of the zinc ions. Based on these data, our future work will focus on investigating various electrodes and electrolytes in ARZIB systems.

5. References
[1] Kohler J, Makihara H, Uegaito H, Inoue H and Toki M 2000 Electrochim. Acta 46 59
[2] Wang G, Fu L, Zhao N, Yang L, Wu Y and Wu H 2007 Angew. Chem. 119 299
[3] Luo J Y, Cui W J, He P and Xia Y Y 2010 Nature Chemistry 2 760
[4] Whitacre J F, Tevar A and Sharma S 2010 Electrochem. Comm. 12 463
[5] Wu X, Cao Y, Ai X, Qian J and Yang H 2013 Electrochem. Comm. 31 145
[6] Soloveichik G L 2011 *Annu. Rev. Chem. Biomol. Eng.* 2 503
[7] Wang H, Huang K, Zeng Y, Yang S and Chen L 2007 *Electrochim. Acta* 52 3280
[8] Wu X Y, Sun M Y, Shen Y F, Qian J F, Cao Y L, Ai X P and Yang H X 2014 *ChemSusChem* 7 407
[9] Zhang B, Liu Y, Wu X, Yang Y, Chang Z, Wen Z and Wu Y 2014 *Chem. Commun.* 50 1209
[10] Liu Z, Pulletikurthi G and Endres F 2016 *ACS APPL. Mater. Interfaces* 8 12158
[11] Yan J, Wang J, Liu H, Bakenov Z, Gosselink D and Chen P 2012 *J. Power Sources* 216 222
[12] Zhang H, Wu X, Yang T, Liang S and Yang X 2013 *Chem. Commun.* 49 9977
[13] Zhang L, Chen L, Zhou X and Liu Z 2015 *Adv. Energy Mater.* 5 1400930
[14] Trócoli R and La Mantia F 2015 *View issue TOC* 8 481
[15] Wang R Y, Wessells C D, Huggins R A and Cui Y 2013 *Nano Lett.* 13 5748
[16] Xu C, Li B, Du H and Kang F 2012 *Angew. Chem. Int. Ed.* 51 933
[17] Lee B, Yoon C S, Lee H R, Chung K Y, Cho B W and Oh S H 2014 *Sci. Rep.* 4 6066
[18] Karyakin A A 2001 *Electroanalysis* 13 813
[19] Pasta M, Wang R Y, Ruffo R, Qiao R, Lee H W, Shyam B, Guo M, Wang Y, Wray L A, Yang W, Toneye M F and Cui Y 2016 *J. Mater. Chem. A* 4 4211
[20] Sun X, Duffort V and Nazar L F 2016 *Adv. Sci.* 3 1600044
[21] Wang R Y, Shyam B, Stone K H, Weker J N, Pasta M, Lee H W, Toney M F and Cui Y 2015 *Adv. Energy Mater.* 5 1401869
[22] Lee C and Jeong S 2016 *Chem. Lett.* 45 1447
[23] Pavlov M, Siegbahn E M and Sandström M. 1998 *J. Phys. Chem. A* 102 219
[24] Hartmann M, Clark T and Eldik R V 1997 *J. Am. Chem. Soc.* 119 7843
[25] Kameda Y, Saitoh H and Uemura O 1993 *Bull. Chem. Soc. Jpn.* 66 1919
[26] Hou Z, Zhang X, Li X, Zhu Y, Liang J and Qian Y 2017 *J. Mater. Chem.* 5 730

**Acknowledgments**

This work (Grants No.C0502212) was supported by Business for Cooperative R&D between Industry, Academy, and Research Institute funded Korea Small and Medium Business Administration in 2017. This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. NRF-2017R1A2B4010544).