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Rechargeable Zinc-Ion Battery Based on Choline Chloride-Urea Deep Eutectic Solvent

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Recently, because of their cost effectiveness, high safety and environmental friendliness, zinc-ion batteries (ZIBs) are receiving enormous attention. Until now, aqueous-based ZIBs have been the focus of attention. However, the issues regarding hydrogen evolution, and zinc electrode passivation as well as dendrite formation limit their practical application. In this work, a biocompatible, stable and low-cost choline chloride/ urea (ChCl/urea) deep eutectic solvent is reported as an alternative electrolyte for rechargeable ZIBs based on delta-type manganese oxide (δ -MnO₂) intercalation electrode. The behavior of the zinc electrode on stripping and deposition in ChCl/urea electrolyte was examined. Besides, the charge storage and charge-transfer characteristics of the battery was studied. The results showed that there was no sign of dendrite formation on the zinc electrode during long-term cycling. Consequently, the fabricated battery exhibited good electrochemical performance with the maximum specific capacity of 170 mAh/g and good cyclability. In addition, the system showed reversible plating/stripping of zinc (Zn) without dendrite formation and no passivation layer on the zinc electrode. Hence, the results confirmed the reversible intercalation of Zn from the deep eutectic solvent ChCl/urea into the δ -MnO₂ electrode. Overall, the proposed electrolyte shows good promise for Zn/ δ -MnO₂ battery system. © The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0641906jes]

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It is noted that the development of clean, safe and low-cost electrical energy storage systems (ESSs), particularly batteries, has attracted much attention. This is due to an increase in the degree of electrification in various applications, namely portable electronic devices, electric appliances and electric vehicles.^{1–3} Although many batteries, such as the lithium-ion battery (LIB), lead-acid battery and nickelmetal hydride battery (Ni-MH), have been commercialized already, they are still expensive. Besides, there are concerns regarding toxic and safety issues and raw material supply.^{4,5} Thus, the challenge for battery development is to find a battery system that meets both economic and environmental demands. Presently, a rechargeable zinc-ion battery (ZIB) using a manganese oxide (MnO₂) intercalation electrode is regarded as the most promising system.⁶ This battery can be fabricated via LIB manufacturing process but uses a much cheaper raw material.⁷

Compared with other electrode materials, both zinc (Zn) and MnO₂ are abundant, environmentally benign and relatively cheap.⁸ Zn also provides a very high specific capacity of 820 mAh/g. In recent years, aqueous-based ZIBs have been the focus of attention. This system exhibits a specific capacity above 200 mAh/g with a nominal voltage around 1.1–1.3 V.⁹ Besides, ZIBs with aqueous electrolytes have a number of advantages i.e. high-energy density, high-safety and good stability over a large number of cycles and are environmentally friendly. Nevertheless, they suffer from other issues, such as hydrogen evolution, electrolyte decomposition due to the narrow potential window of water (~1.23 V) and Zn electrode passivation which reduces battery performance.^{10–12} Therefore, ZIBs using non-aqueous electrolytes, exhibiting a wide operating voltage window and high reversibility of Zn deposition and dissolution, have been proposed to address these issues.¹³

A polar-aprotic electrolyte, such as acetonitrile (AN), is one of the most extensively studied.^{14,15} It provides a wide electrochemical window (up to \sim 3.8 V) and when combined with Zn(CF₃SO₃)₂ or Zn(TFSI)₂, it offers efficient plating and stripping of Zn (columbic

efficiency > 99%).¹⁶ Sang-Don et al. (2017) investigated ZIBs using δ -MnO₂ electrode and AN with Zn(TFSI)₂ electrolyte.¹⁷ This system delivered a maximum specific capacity of 123 mAh/g and more than 99% of columbic efficiency. However, despite its good performance, it was noted that there was significant capacity fading caused by passivation at the electrode surface. Furthermore, there was a report of using AN with other ZIB systems: e.g. Zn/ZnAl_xCo_{2-x}O₄,¹⁵ Zn/V₃O₇·H₂O¹⁸ and Zn/PBA.¹⁴ Nonetheless, AN was found to be flammable, toxic and very volatile which decreased the overall stability of the batteries.

Another viable alternative electrolyte was to use a room temperature ionic liquid (RTIL) electrolyte which consisted of cations and anions. Over the past decades, RTIL, as an electrolyte, proved to be extremely interesting for the electroplating of metals.¹⁹ RTIL had several attractive properties, such as high ionic conductivity, high electrical stability and low vapor pressure.²⁰ Traditional RTIL, imidazoliumbased ionic liquid, demonstrated a great performance of Zn electrodeposition and an outstanding electrochemical window (above 4 V).²¹ Therefore, it seemed to be a good choice for battery applications. Nevertheless, it proved to be costly and highly sensitive to moisture, making batteries using RTIL infeasible to produce on a large-scale.²² There are only a few reports of imidazolium-based RTIL applications as regards ZIBs.^{23–25}

An alternative class of RTIL, namely a deep eutectic solvent (DES), was formed from a mixture of quaternary ammonium salts i.e. choline chloride (ChCl) and a hydrogen-bond donor. This combination was found to be both air and moisture stable. DES provided many advantages over traditional RTIL since DES was of low toxicity, low-cost and biodegradable.²⁶ Due to its large metal-salts solubility, ChCl/urea is one of the most promising DES systems which is crucial for efficient platting and stripping of metals and provides a wide electrochemical window (up to ~2.54 V for dry solvent).²⁷ Several studies have reported the use of ChCl/urea combined with anhydrous ZnCl₂ for the Zn electrodeposition to obtain the nano-porous structure of Zn; some focus on its deposition mechanism.^{22,28} However, the real mechanism of Zn electrodeposition in this system has not been clearly described. The most precious conclusion reached was that the nucleation of Zn during the deposition strongly depended upon the structure of an

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electrical double layer in the liquid caused by the presence of ZnCl₂.²⁹ Besides, to the best of our knowledge, the application of DESs in ZIBs has never been reported.

Herein, this study focuses on investigating the performance and feasibility of using ChCl/urea DES as the electrolyte for ZIB with MnO₂ intercalation electrode. In an effort to maximize the performance, delta-type manganese oxide (δ -MnO₂) was chosen for this work due to the crystallographic water inside the δ -MnO₂ structure which has a crucial role in reducing the desolvation energy of intercalation reaction.¹⁶ Furthermore, the stripping and deposition behavior of Zn electrode in ChCl/urea electrolyte was examined. Galvanostatic cycling (charge-discharge), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques were applied to investigate the charge storage and charge-transfer characteristic of the batteries.

Experimental

Materials.—Choline Chloride $(HOC_2H_4N(CH_3)_3^+Cl^-, ChCl, 98.0\%)$ was purchased from Sigma-Aldrich. Potassium permanganate (KMnO₄, 99.0%), Urea (CH₄N₂O, 98.0%), zinc sulfate heptahydrate (ZnSO₄.7H₂O, 99.0%) and zinc chloride (ZnCl₂, 98.0%) were purchased from Ajax Finechem. Dimethylformamide (DMF, 98.0%) was purchased from Carbot Corp. Manganese(II) sulfate monohydrate (MnSO₄.H₂O, 99.0%) was purchased from QReC. Poly(vinylidene fluoride) (PVDF, MW ~180,000) was purchased from Sigma-Aldrich. Ni-foam (0.5 mm thick, 100 PPI) was purchased from Qijing Trading Co., Ltd. Glass microfiber (Whatman 1822-047 GF/C, 1.2µm) was purchased from SGL Group. Zn sheet (99.99%) was purchased from Sirikul Engineering Ltd., Part.

Electrolyte preparation.—The ChCl/urea based deep eutectic solvent was formed by ChCl with urea, at the eutectic composition, in a ratio of 1:2 by moles under controlled temperature of 70°C, until it all melted together. The preparation was conducted inside a nitrogen filled glove box (< 0.5 ppm H₂O) to prevent the contamination of moisture from the ambient air. Then, ZnCl₂ was added at 0.3 M concentration. The resultant solution was a clear, medium viscous liquid. Herein, the prepared electrolyte is referred as 12CU: 0.3M ZnCl₂.

Delta-type *MnO*₂ *preparation.*—A delta-type manganese oxide (δ -MnO₂) nanosheet was synthesized by a simple hydrothermal method.³⁰ 0.948 g KMnO₄ was dissolved in 35 mL of deionized (DI) water and vigorously stirred. Then, 0.169 g MnSO₄.H₂O was added to the solution and left for 30 min; again, the solution was vigorously stirred. Next, the solution was loaded into a Teflon-lined stainless-steel autoclave and heated at 160°C for 24 h. Subsequently, the product was filtered, washed many times with DI water and then dried overnight at 70°C under vacuum. X-Ray Diffraction (XRD) analysis was used to confirm that the synthesized sample was δ -MnO₂.

Electrode preparation and cell fabrication.—δ-MnO₂ electrodes (discharge cathodes) were prepared by slurry mixing of synthesized δ-MnO₂, conductive carbon black, PVDF in a ratio of 7:2:1 by weight in DMF. Then, the slurry was coated onto carbon cloth by a lab coating machine (AOT-FCM-250, AOT Electronic Technology Co., LTD) and dried at 70°C under vacuum. The dry weight of loading material was around 3 mg/cm². Zn electrodes (discharge anodes) were prepared by electrodeposition of Zn from 1 M ZnSO₄ aqueous solution onto Ni-foam using Zn sheet as a counter electrode at the current density of 50 mA/cm². The weight of zinc loaded was 20 mg/cm². Both electrodes were punched into a 15 mm diameter disk. A glass microfiber was punched into a 19 mm disk and used as the separator. Then, 0.3 mL of electrolyte was added to the cell. The testing cells were fabricated as a coin cell (CR2032). The structure of the CR2032 cell is shown in Fig. 1. During discharge, the Zn electrode serves as



Figure 1. Schematic diagram of CR2032 coin cell configuration.

the anode whilst MnO_2 electrode functions as the cathode (Fig. 2a). Consequently, electrochemical dissolution of the Zn electrode (oxidation of Zn) in ChCl/urea DES occurs; insertion of Zn^{2+} species from the electrolyte takes place at the MnO_2 cathode. In comparison, during recharge, the Zn electrode and MnO_2 electrode function as the cathode and anode, respectively (Fig. 2b). Both the extraction of Zn^{2+} species from the MnO_2 electrode as well as the deposition of Zn (reduction of Zn) onto Zn electrode take place simultaneously. Therefore, Zn/Zn^{2+} deposition/stripping on Zn electrode and insertion/extraction on MnO_2 electrode enables the battery to repeatedly store/deliver electrical energy.

Electrochemical and material characterization.—Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed via a potentiostat/galvanostat with an impedance measurement unit (AMETEK, PAR VersaSTAT 3A). Galvanostatic cycling of the battery was carried out by a battery analyzer (NEWARE BTS-4000 series). The structure and morphology of the electrodes were investigated using a scanning electron microscope (SEM; JEOL, JSM-5800LV). X-ray diffraction analysis was carried out using an X-ray diffractometer (XRD; Bruker, D2 PHA- SER) with Cu K α radiation at 2 θ from 10 to 70°. To characterize the electrode after use, the electrodes were disassembled from the cell and washed with DI water repeatedly to remove the electrolyte. Then, the electrode was dried overnight at 70°C under vacuum.

Results and Discussion

Zinc plating and stripping.—The reversible plating/stripping of Zn is one of the most important aspects of the Zn electrode for ZIBs. The electrolyte ChCl/urea deep eutectic solvent with ZnCl₂ contains chlorozincate ([ZnCl₄]^{2–}) as a Zn containing species. This species has an important role in the double-layer structure during the Zn



Figure 2. Schematic diagram of the battery: a) battery during discharge (Zn anode and MnO_2 cathode), and b) battery during recharge (Zn cathode and MnO_2 anode).



Figure 3. Electrochemical performance of Zn stripping and plating (Zn|electrolyte|Zn cell): a) galvanostatic charge-discharge at 0.1, 0.2, 0.5, and 1.0 mA/cm², b) CV at a scan rate of 10 mV/s from -0.5 to +0.5 V, and c) SEM image of Zn electrode deposited after the 150th cycle.

deposition process. According to the work of Abbott et al. (2011),³¹ critical concentration of ZnCl₂ is required for the deposition of Zn from this mixture. Hence, 0.3 M $ZnCl_2$, which is above the critical concentration, was chosen for our study. The long-term cycling behavior of the Zn electrode was examined using a Zn electrolyte Zn cell, where the prepared Zn electrodes were used as both positive and negative electrodes. The cell was cycled for 10 cycles at 0.1, 0.2, 0.5, and 1.0 mA/cm² for 30 min at each current density. The results are displayed in Fig. 3a. During cycling, at each current density, the polarization voltage at each current density was bounded by the maximum and minimum voltages. Also, the maximum voltages did not increase upon the cycling indicating that no passivation layer takes place on the Zn surface. In addition, the CV experiment of the Zn electrode was performed using the two-electrode configuration at a scan rate of 10 mV/s and potential range of -0.5 to +0.5 V (vs. Zn/Zn²⁺ in 12CU: 0.3M ZnCl₂) using the Zn|electrolyte|Zn cell. In this configuration, the prepared Zn electrodes were used as the working and counter electrodes. Also, the counter electrode was used as the reference electrode. The cyclic voltammogram of Zn plating/striping is shown in Fig. 3b. The charge-transfer ratio of plating/stripping between the testing range was calculated to be 0.98, indicating that the deposition and dissolution process is highly reversible. We further investigated the behavior of the long-term cycling behavior of the Zn electrode. The cell was cycled for 150 cycles at 1.0 mA/cm² for 30 min. Fig. 3c shows the morphology of Zn deposited after the 150th cycle. The grain size was found to be ~ 100 nm. This small grain size corresponds to the fast rate of nucleation whereas the bulk growth was slow.³² Besides, there was no sign of dendrite formation on the Zn electrode during a long-term cycling.

Battery performance.—A galvanostatic (constant-current) cycling test of the battery was performed using a $Zn|e|ectrolyte|\delta-MnO_2$ cell. In this cell, the prepared Zn electrode was used as the negative electrode whilst the prepared $\delta-MnO_2$ was used as the positive

electrode. The battery exhibited an open-circuit voltage of ~ 1.5 V as-prepared. The rate performance test was conducted by discharging the battery until it reached the lower cutoff voltage of 0.4 V. Then, charging continued until it reached a higher cutoff voltage of 1.9 V. The cell was tested at various current densities of 50, 100, 150, and 200 mA/g of δ -MnO₂ for 10 cycles at each current density. Fig. 4a illustrates the rate performance of the battery from the 1st cycle to the 50th cycle. The cell exhibited an initial discharge capacity of 170 mAh/g while the capacity at the 2nd, 3rd, 4th and 5th were 133, 114, 99 and 92 mAh/g, respectively. Thus, in the 10th cycle, the capacity reached a stable plateau at \sim 90 mAh/g. The large capacity, fading in the first five cycles may be due to the high solubility of δ -MnO₂ in the electrolyte (493 ppm at 60°C).³³ Unfortunately, there is no reported of such a value at ambient temperature. However, the dissolution of cathode materials could change the surface structure and the surface properties by forming SEI layer which leads to the less reversibility of the cathode reaction.³⁴ In comparison to other $Zn|\delta$ -MnO₂ cells previously reported, the proposed ChCl/urea system exhibited the maximum specific capacity of 170 mAh/g which was found to be significantly higher than that of the non-aqueous AN/Zn(TFSI)2 system (123 mAh/g, 0.05-1.9 V).¹⁷ However, it was lower than that of the aqueous-based system (252 mAh/g, 1.0–1.8 V).³⁵ The higher capacity of the aqueous-based system was due to the conversion reaction of Zn^{2+} with MnO₂ to form Mn(III) species, such as ZnMn₂O₄ which has poor reversibility. Moreover, the operating voltage of aqueous-based system overlaps with the potential window of water (~ 1.23 V).¹¹ Thus, the charge transfer of this system may contribute to the decomposition of water, which leads to the significant degradation of the cell upon the cycling.

The capacity, observed at different current densities, was 72 mAh/g at 100 mA/g, 63 mAh/g at 150 mA/g and 51 mAh/g at 200 mA/g. Subsequently, the current density was switched back to 50 mA/g. Thus, the capacity was found to be 85 mAh/g which was slightly lower than the value observed at the 10^{th} cycle.



Figure 4. Electrochemical performance of the battery (Zn|electrolyte| δ -MnO₂ cell): a) rate performance of the battery at 50, 100, 150, and 200 mA/g, b) cycling behavior at current density of 100 mA/g from 51st to 150th cycle, c) CV at a scan rate of 0.5 mV/s from 0.4 to 1.9 V, and d) charge-discharge profile at 50, 100, 150, and 200 mA/g.

Fig. 4b shows the cycling behavior of the cell at the current density of 100 mA/g. During cycling, a slight decrease in the capacity was observed. The fading rate was calculated to be 0.7% per cycle. This capacity loss may correspond to the change in the contact surface between the δ -MnO₂ electrode materials and the current collector after a long-term cycling. The fading rate of ChCl/urea system is similar to those in the cases of aqueous/ZnSO₄ and AN/Zn(TFSI)₂ electrolytes. Nevertheless, the primary cause of the capacity fading is different. It was reported that the capacity fading in the aqueous system results from the formation of irreversible ZnMn₂O₄ at the cathode.³⁵ In comparison, ZnMn₂O₄ was found to be reversible in the AN system.¹⁷ The capacity fading resulted from the formation of ZnO on the cathode surface was reported.

Fig. 4c shows the cyclic voltammogram of the δ -MnO₂ electrode. The CV experiment was conducted on the same battery at the 10th cycle with the potential range from 0.4 to 1.9 V and a scan rate of 0.5 mV/s in order to observe the charge-transfer characteristic of the δ-MnO₂ electrode. Also, the CV experiment was carried out using the two-electrode configuration where the positive (δ -MnO₂) electrode and the negative (Zn) electrode were connected as the working and the counter electrodes, respectively. Besides, the counter electrode was used as the reference electrode. The reduction reaction started from the open-circuit potential of 1.69 V and reached the peak at 0.97 V; this may be attributed to the insertion of Zn^{2+} into the MnO₂ host material. Subsequently, the oxidation peak occurred at 1.51 V which refers to the Zn^{2+} extraction from the δ -MnO₂ host material. In addition, the high background current may correspond to the high capacitance effect during the charge-transfer reaction. This characteristic is consistent with the results, as observed in Fig. 4d. At low current density, the cell behaved like a typical metal-ion intercalation battery, while at high current density, the voltage is linearly proportional to the capacity (capacitor-like behavior).³⁶ This hybrid behavior of the latter corresponds to the electrolyte structure. As an ionic liquid contains various cations and anions, the adsorption of unreacted-species onto the electrode surface resulted in the high capacitance current.

The polarization of voltage, with respect to the specific capacity, was observed to be steeper as compared with the aqueous-based system. This was due to higher overpotential when the reaction occurred and corresponds to the lower ionic conductivity in contrast to the aqueous electrolyte.

Also, as shown above in Fig. 4d, only one discharge plateau is depicted, indicating that there was just one reaction occurring on the δ -MnO₂ electrode, similar to that observed in the AN/Zn(TFSI)₂ system. In comparison, the aqueous-based system involved two discharge plateaus.³⁵ The first one was Zn intercalation which formed a layered Zn_xMnO₂. The second one was the conversion reaction which produced ZnMn₂O₄.

To further investigate the change in the charge-transfer characteristic of the battery, EIS technique was performed using the twoelectrode configuration with potentiostatic EIS mode. The EIS experiments were carried out at the as-prepared, at the 1st cycle, and at the 130th cycle of the galvanostatic test, in the frequency range of 100 kHz to 10 mHz and amplitude potential of 10 mV. Fig. 5a shows the equivalent-circuit model describing the charge-transfer characteristic of the cell. In this model, the first horizontal-axis intercept (R_0) , the high-frequency semicircle (R1, CPE-1), the low-frequency semicircle $(R_2, CPE-2)$ and the 45° inclined-straight line (W) can be assigned to: the internal resistance, the reaction at negative electrode, the reaction at positive electrode and the diffusion of Zn species in the $\delta\text{-MnO}_2$ electrode materials, respectively.³⁷ As shown in Fig. 5b, it is important to note that the size of R_1 and R_2 refers to the charge-transfer resistance of the negative and positive electrode. Besides, the size of W (Warburg coefficient) is inversely proportional to the square root of guest-species diffusivity in the host materials. The interested parameters which included R₀, R₁, R₂ and W were determined via ZSimpWin version 3.20. The modeling results are shown in Table I. According to the impedance spectra shown in Fig. 5c and the parameters presented in Table I, after the first cycle, the diameters of the low-frequency semicircle (or R2) and W decreased. It implies that there was a lowering in activation energy of Zn insertion caused by better mass transport



Figure 5. Potentiostatic impedance spectra of the δ -MnO₂ electrode with testing frequency range of 100 kHz to 10 mHz and amplitude of 10mV: a) equivalent circuit used to simulate the impedance spectra, b) schematic diagram describing the component of impedance spectra, c) EIS of the before/cycled electrode, and d) EIS of the fully charged and discharged electrode at the 10th cycle.

in the δ -MnO₂ electrode, while R₀ and R₁ were almost the same. After the 130th cycle, all parameters were observed to be higher than those of the 1st cycle. The increase in R₀ related to the change in electronic contact, such as the deterioration of the polymeric binder which binds the active materials and the current collector together. The change in R₁ may correspond to the change in the morphology of Zn surface after the long cycling. However, the increase in R₂ and W may be due to the fact that some part of the intercalated electrode was not reversed back when charging. Therefore, the amount of the available site for the intercalation of Zn^{2+} species was degraded. Further EIS experiments of the cell at fully charged and discharged state were conducted. The results are as shown in Fig. 5d. At discharge state, the low-frequency semicircle increased in size more than those at fully charged state. Moreover, the length of the inclined-straight line was found to be longer, indicating that the charge-transfer resistance R2 increased while the diffusivity decreased when the intercalated electrode took place. Thus, it is deduced that the irreversible intercalated part had an important role in the increase of R₂, resulting in the capacity fading upon cycling.

Also, SEM was used to examine the change of the δ -MnO₂ electrodes after 5th and 150th cycle. The SEM results of the 5th and 150th cycle are shown in Figs. 6a and 6b, respectively. After long cycling, the cracks are clearly seen indicating the destruction of polymer binder network upon the cycling. However, the nanostructure of the cathode materials was not significantly changed. It means the change in the charge storage performance of battery may result from the cracking of

Table I. EIS parameters obtained by fitting the data to equivalent circuit models.

$\mathrm{R}_0~(10^{-1}~\Omega)$	$R_{1}\left(\Omega\right)$	$\mathrm{R}_2~(10^{-2}~\Omega)$	$W(10^{-2})$
1.699	8.065	1.430	1.113
1.795	7.217	0.319	0.743
2.635	10.270	1.081	1.745
	$\begin{array}{c} R_0 \ (10^{-1} \ \Omega) \\ \hline 1.699 \\ 1.795 \\ 2.635 \end{array}$	$\begin{array}{c} R_0 (10^{-1} \Omega) & R_1 (\Omega) \\ \hline 1.699 & 8.065 \\ 1.795 & 7.217 \\ 2.635 & 10.270 \end{array}$	$\begin{array}{c c} R_0 (10^{-1} \Omega) & R_1 (\Omega) & R_2 (10^{-2} \Omega) \\ \hline 1.699 & 8.065 & 1.430 \\ 1.795 & 7.217 & 0.319 \\ 2.635 & 10.270 & 1.081 \end{array}$

the binding materials rather than the structural change of the δ -MnO₂ particles. The cracking of cathode affects the electronic conductivity of the cell which increases overpotential of the electrode. Hence, it leads to significant fading of the capacity after long cycling. The results are in line with those observed with EIS.

Fig. 7a shows the XRD pattern of the prepared δ -MnO₂ nanosheet. The characteristic peaks i.e. (001), (002), (11-1) and (31-2), observed at 2 θ , were namely, 12.5°, 25°, 36.5° and 65.3°, suggesting the sample is δ-MnO₂³⁰ Furthermore, the as-prepared electrode was characterized. The observed additional peaks at 26° and 43° are ascribed as the characteristic peaks of the current collector, such as carbon cloth.³⁸ The δ -MnO₂ electrodes were collected from the cell at fully charged and discharged state of the 10th cycle, for the ex-situ XRD experiments in order to observe the structure changing upon the discharging. According to Fig. 7b, after discharge, the intensity of the characteristic peaks of δ -MnO₂ at (001) and (002) decreased significantly. In addition, a small shift back of the peak (11-1) was observed. This may correspond to the change in the unit cell parameters. Nonetheless, the overall structure is still almost the layered structure. Besides, the peaks of ZnMn₂O₄ were not observed. Thus, the behavior of Zn intercalation on the MnO₂ electrode was similar to that of AN/Zn(TFSI)₂ system reported by Sang-Don et al. (2017).¹⁷ Consequently, the existence of



Figure 6. SEM images of δ -MnO₂ electrodes at a) 5th cycle, and b) 150th cycle.



Figure 7. The XRD patterns of the positive electrode: a) as-prepared δ -MnO₂ nanosheet, and b) as-prepared electrode, fully charged electrode and discharged electrode.

the layered Zn_xMnO_2 was confirmed. Besides, the main reactions of the proposed battery system can be expressed as:

Negative electrode reaction: $xZn + 4xCl^{-} \leftrightarrow x[ZnCl_4]^{2-} + 2xe^{-}$

Positive electrode reaction: $x[ZnCl_4]^{2-} + MnO_2 + 2xe^- \leftrightarrow$

 $Zn_xMnO_2 + 4xCl^-$

Overall reaction: $xZn + MnO_2 \leftrightarrow Zn_xMnO_2$

In the proposed system, during discharge, Zn dissolution occurs at the negative electrode. Then, Zn^{2+} coordinates with chloride anion (Cl⁻) to form [ZnCl₄],²⁻ acting as a charge-transfer species and carrying Zn^{2+} to the positive electrode. Thus, Zn^{2+} at the positive electrode intercalates into the δ -MnO₂ structure and forms Zn_xMnO_2 . During recharge, extraction of Zn^{2+} from Zn_xMnO_2 takes place at the positive electrode and forms [ZnCl₄].²⁻ Further, [ZnCl₄]²⁻ transfers across the cell to the negative electrode. At the same time, the deposition of Zn from [ZnCl₄]²⁻ occurs onto the negative electrode. The reaction mechanism is similar to what was reported in AN/Zn[TFSI]₂ electrolyte system.¹⁶

Conclusions

In this study, a biocompatible, stable and low-cost ChCl/urea deep eutectic solvent has been reported as an alternative electrolyte for rechargeable zinc-ion batteries based on a δ -MnO₂ intercalation electrode. Herein, the work demonstrated that intercalation of Zn²⁺ from the deep eutectic solvent ChCl/urea into the δ -MnO₂ electrode is reversible. Besides, the formation of the irreversible product ZnMn₂O₄, on the δ -MnO₂ electrode during discharging was not observed. Consequently, the fabricated battery exhibited good electrochemical performance, including high specific capacity and good cyclability. In addition, this system showed the reversible plating/stripping of Zn without a sign of dendrite formation and passivation on the zinc electrode. The results indicated that the ChCl/urea electrolyte is promising for the Zn/ δ -MnO₂ battery system.

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