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A Conceptual Magnesium Battery with Ultrahigh Rate Capability[†]

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A new type of rechargeable Mg battery is demonstrated, which achieves charge transfer through simultaneous transport of Mg²⁺ cations and halogen anions during electrochemical cycling. The novel Mg/AgCl battery shows remarkable rate capability up to 10 C and excellent cyclability at high rates, with a flat plateau at 2 V.

Rechargeable Li-ion batteries have become common energy storage devices for portable electronics. However, cost, power and durability concerns prevent the batteries from rapid and extensive use in large scale applications, such as electric / hybrid vehicles as well as smart grids. Recently, some promising batteries with other light weight ions such as Na⁺, Mg²⁺ or Al³⁺, have created considerable interests to overcome the challenges and to share the responsibilities with Li-ion batteries.¹⁻¹¹ Among them, the Mg system is an interesting candidate, because of i) cost-effective Mg compounds based on its earth abundance and ii) high durability originated from the non-preferable metal dendrite formation for Mg,⁶ compared with Li. Despite its promising future, the research of rechargeable Mg battery remains a challenge. The major hurdle is that the intercalation chemistry, which shows great success in the Li-ion battery, is not well applicable to the Mg battery. Because of the divalent nature of Mg²⁺ ions, the insertion and extraction generate strong electrostatic interaction with the ions in the host lattice, and prevents fast Mg²⁺ diffusion.¹²⁻¹⁴ The diffusivity of Mg²⁺ ions can be orders of magnitude lower than that of Li⁺ ions in the same host matrix, therefore it limits the rate capability (power) of intercalation cathodes, or even the practical insertion of Mg²⁺ ions.¹⁴ To date, the Chevrel phase Mo₆S₈ is the only reported intercalation cathode with high cyclability and reasonable rate capability, because its structure contains unique Mo₆ clusters which can easily compensate for the charge imbalance due to the introduction of bivalent ions, and achieves faster Mg²⁺ intercalation kinetics.^{5,12}

An alternative solution to secure practically high rate capability is to utilize another unique redox reaction on the cathode side that replaces the intercalation reaction and balances the electron transfer. Here, we present a novel concept for ultra-high rate capability in the rechargeable Mg battery, where the charge transfer is achieved via simultaneous transport of Mg²⁺ cations and Xⁿ⁻ (herein, halogen) anions during electrochemical cycling (ESI Figure S1). A key point is that the charge balance derived from Mg²⁺ and Xⁿ⁻ is compensated in the electrolyte media, resulting in its electroneutrality. The cathode of this battery only experiences the formation and

decomposition of metal halide during cycling, while Mg plating and stripping only occur on the anode side. The diffusion of monovalent halogen anion in the cathode should be significantly faster than that of divalent Mg²⁺ cation; therefore high rate capability is expected.

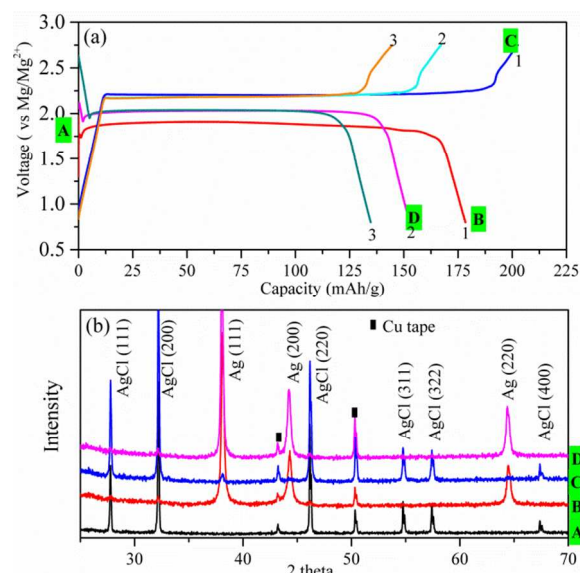


Figure 1 (a) Galvanostatic curves for the Mg/AgCl battery. The green bars show the electrochemical states of the cathodes taken for X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Scanning electron microscopy (SEM). (b) XRD patterns of the AgCl cathodes at different electrochemical states. Cu tape was used to fix the samples during XRD scan.

Our conceptual Mg battery consists of metallic Mg as the anode, AgCl as the cathode, and 0.2 M phenyl magnesium chloride mixed with aluminium trichloride (PhMgCl-AlCl₃) in tetrahydrofuran (THF) solution as the electrolyte. The PhMgCl-AlCl₃/THF electrolyte is well known to be compatible with Mg metal, showing high coulombic efficiency of Mg deposition and dissolution.^{4,7} Also, it has been found that the mobile Cl⁻ anion species extensively exists in the solution in many forms and cause serious corrosion against metal current collectors such as Al and stainless steel.^{15,16} Herein, we conversely utilized Cl⁻ as the mobile anion for redox reaction in this cell. The cathode material AgCl/carbon composite was prepared by a precipitation reaction between AgNO₃ and HCl (ESI Figure S2). Scanning electron microscopy (SEM) observation indicated the precipitated AgCl was composed of primary particles of approximately 100 nm, which aggregated to micron-sized secondary particles homogeneously embedded in the carbon matrix (ESI Figure S3).

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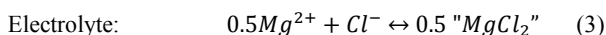
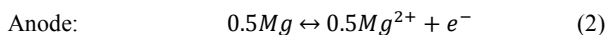
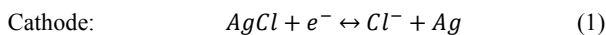
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Figure 1 (a) shows the galvanostatic curves of the Mg/AgCl battery operated at a rate of 0.12 C (9.4 mA/g). A flat plateau around 2.0 V is repeatedly observed at both charge-discharge profiles. A specific capacity of 178 mAh/g is achieved in the first discharge, which is 95.4% of the theoretical capacity of AgCl. The slightly lower plateau in the first discharge might be associated with an activation process of AgCl, as clearly evidenced by a noticeable morphology and size change of the AgCl particle after the first discharge process (ESI Figure S4). After the initial process, the morphology of the cathode particles kept unaltered without notable changes in subsequent cycles. This microscopic change at the initial discharge may enhance the charge transfer between active material and electrolyte, which narrows down the polarization between charge and discharge.¹⁷ Starting from the second cycle, the polarization is only about 0.1 V. This value is much lower than those of other reported Mg battery cathodes.^{7,8,18,19}

An ex-situ X-ray diffraction (XRD) study was performed to investigate the electrochemical process in the cathodes ended at different electrochemical states (Figure 1 (b)). The pristine electrode (A) is composed of pure AgCl without any impurity peaks observed in the XRD pattern. The discharged electrode (B) is completely indexed to metallic Ag showing no AgCl peak. This indicates the discharge reaction on the cathode is the decomposition of AgCl which forms metallic Ag after discharge. After the charge process (C), the AgCl phase is recovered, although some minor peaks related to Ag still remain. After the second discharge (D), the cathode changes again to metallic Ag. The reversible redox reaction of the Ag element was also verified by XPS measurements (ESI Figure S5), which clearly demonstrate the transition between Ag⁺ and metallic Ag during the cycling.

We also examined whether the anode reaction follows Mg deposition and dissolution during cycling. To avoid a dominant signal derived from Mg foil as an anode, the Mg anode is replaced with stainless steel (SS) after an initial complete discharge. The reconstructed cell was cycled very well and showed the same voltage plateau as that in Figure 1 (a) (ESI Figure S6). The SS electrode was examined with ex-situ XRD after recharge and second discharge (ESI Figure S7). Consistent with our expectations, the recharged steel electrode showed the deposition of metallic Mg which disappeared after second discharge process. It is, thus, concluded the electrochemical reaction during the operation of this battery is the decomposition and formation of metal chloride on the cathode, married with the dissolution and deposition of metallic Mg on the anode.

Based on the above-described results, electrochemical reactions should be drawn as follows:



where "MgCl₂" is unique complex species in the non-aqueous electrolyte system. It has been proven that the electrolyte has many species, specifically MgCl⁺, Mg₂Cl₃⁺, MgCl₂, etc., and all of them are coordinated by THF through multiple equilibrium reactions.^{4,7,20} In our study, both Mg²⁺ and Cl⁻ from electrodes must form those species in the same way. We also notice that the discharge process in this conceptual battery is similar to that of the magnesium seawater-activated batteries.²¹ However, those batteries are not practically rechargeable, whereas our conceptual battery is with current configuration (excessive anode and electrolyte). A significant point is the compatibility of electrolyte with Mg metal. In the seawater battery, the incompatibility between water and Mg metal anode must be a critical reason for poor rechargeability. Hence, our system,

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designed with non-aqueous electrolytes, enabled recharging with higher working voltage.

As described above, the sluggish diffusion of Mg²⁺ significantly hinders its insertion/extraction in the classical cathode, leading to poor rate capability. The major advantage of our conceptual battery lies on the fact that it does not rely on the intercalation of Mg²⁺ into the cathode host lattice, thus high rate capability is expected. To assess this, an electrochemical rate test was performed. Figure 2 (a) shows the discharge profiles at different C rates after an activation cycle operated at a rate of 0.12 C. The capacity gradually decreases as the applied current increases, but the capacity observed at 10 C still keeps 104 mAh/g (55% of the theoretical capacity). To the best of our knowledge, this is the highest rate capability ever reported for Mg batteries. We also recognize that our proposed concept is close to the concepts which were recently reported as dual-ion batteries and chloride-ion batteries.^{22,23} The observed ultra-high rate performance should thank to high mobility and high reversibility of Cl⁻ anion species even in the complicated electrolyte equilibrium.^{20,24} Continuous research on electrolyte and its combination with anode/cathode must be addressed for further enhancement of the battery performances.

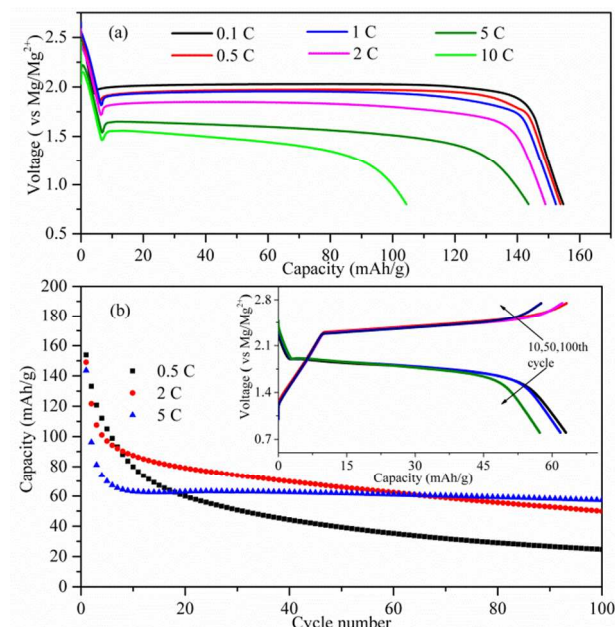


Figure 2 (a) Galvanostatic discharge curves for the Mg/AgCl batteries at different C rates (after one activation cycle). 1 C is equal to 186 mA/g (from the theoretical capacity of AgCl). (b) Cycling behaviors of the Mg/AgCl batteries operated at the 0.5, 2 and 5 C rates. Inset - Selected galvanostatic curves at 5 C rate.

Figure 2(b) shows the cycling performances of the batteries operated at the rates of 0.5, 2 and 5 C after the activation cycle. Inset figure shows the selected discharge-charge profiles observed at the 5 C rate. Even at the 5 C rate, the cell can run well with flat voltage profiles and the discharge capacity retains about 65mAh/g over 100 cycles. Interestingly, in this cell system, the capacity retention was improved with an increase in the C rate. One of the possible reasons would be related with the dissolution of AgCl from the cathode to the electrolyte in spite of its low solubility (0.053 mg/l in THF, ICP measurement) and their migration and deposition onto the anode, which was evidenced from the XRD patterns (ESI Figure S6). At lower C rates, a longer charge time is required, causing greater loss of Ag⁺ ions, consequently resulting in poor cyclability. In addition, electrolyte decomposition, resulting in the consumption of active ions may also cause this behavior. Especially, using excess of Mg

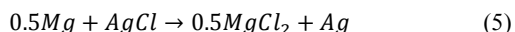
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anode and chloride ion in the electrolyte will cause the loss of those ions to be unobvious and consequently lead better cycling performance at high rate, as shown in our study.

Unlike a classical Li-ion battery, where the electrolyte only facilitates ion transfer and does not participate in the overall reaction, the concentration of the electrolyte in our conceptual battery should change during discharge-charge processes. According to the Nernst equation, the theoretical voltage of the reactions shown in Eqs. 1-3 can be described as follows:

$$V = -\frac{\Delta G}{F} - 0.5 \frac{RT}{F} \ln \left(\frac{a_{Mg^{2+}}(a_{Cl^-})^2}{a_{Mg^{2+}}^0(a_{Cl^-}^0)^2} \right) \quad (4)$$

where $a_{Mg^{2+}}(a_{Cl^-})$ is the activity of Mg^{2+} (Cl^-) in the electrolyte, and $a_{Mg^{2+}}^0(a_{Cl^-}^0)$ is the activity of Mg^{2+} (Cl^-) in the solid $MgCl_2$. ΔG is the free energy change of the solid state reaction:



The first part on the right side of Eq. 4, $-\Delta G/F$, contributes 2.01 V to the overall voltage. Comparing this number with the experimental voltage profiles (Figure 1 (a)) indicates the contribution of the electrolyte to the voltage should be at most in the order of 0.1 V. Further, it has been found that the battery can sustain long cycle life. Even at 10 C stable discharge/charge plateaus were observed after 200 cycles (ESI Figures S8 and S9). This fact suggests the equilibrium reactions in the electrolyte must be highly reversible; otherwise, the cells would fail after fewer cycles due to the shortage of the electrolyte.

A key concern of this conceptual battery system is the solubility of the metal chloride cathode in the organic electrolyte solvent. In a typical closed cell as described in this study, a soluble metal chloride is not as appropriate as an electrode material, because it continuously dissolves into the electrolyte and the metal accumulates on the anode side. One possible solution is to create an insoluble layer to suppress or impede the dissolution of the cathode. We anticipate this protection technique will enable the usage of other low-cost metal chlorides that are soluble in the electrolyte as choices of cathode materials. On the other hand, once this concept is extended to a flow type battery, soluble active materials could be appropriate. As a result, this concept has a great potential to be applied in both closed and open battery systems based on the properties of the electrode materials. Table 1 lists some metal chlorides and their important physical properties related to this conceptual cell. Theoretically, several of them have high capacity and high operation voltage and thus can be considered as potential cathode candidates for future investigation. Actually, it was demonstrated that some metal chlorides had a great potential to show promising performances even without any optimization the preparation (ESI Figure S10).

Another concern related to our concept is that the energy density of the battery system is relatively low because adequate amount of electrolyte has to be added to dissolve "MgCl₂" as a discharged product. In this study, at least 12 ml of THF solvent for 1 g of AgCl is required. As the result, the theoretical energy density of this cell will be at most 30 Wh/L at present, which is much lower than the typical Li-ion battery. Although there are still room to improve its energy density through optimization of electrolyte and cathode materials (using other metal chlorides), this battery system still cannot compete with Li-ion batteries in the term of energy density. However, we found it has a unique feature of ultrahigh rate capability, which make it can be considered in the practical application such as grid storage. Further optimization is required to improve this conceptual system.

Table 1 Potential metal chlorides as cathode and their solubilities in THF obtained by inductively coupled plasma (ICP) measurement. Theoretical voltages were obtained from Eq. 5. Theoretical properties are compared with the initial discharge performances, which are shown in ESI Figure S10.

Metal chloride	Solubility in THF (mg/l)	Theoretical/Initial Capacity (mAh/g)	Theoretical/Initial Voltage (V vs. Mg)
AgCl	0.053	186 / 178	2.01 / ~2.0
PbCl ₂	0.169	192 / (no data)	1.46 / (no data)
CuCl	10.95	270 / 114	1.90 / ~1.6
NiCl ₂	11.25	413 / 230	1.75 / ~1.3
FeCl ₂	59.7	327 / (no data)	1.55 / (no data)
CuCl ₂	384.5	398 / 60	2.21 / ~1.6
CrCl ₃	518.6	507 / (no data)	1.35 / (no data)

* MgCl₂ has quite high solubility of 26.43×10³ mg/l in THF.

In summary, a new type of Mg battery was reported with successfully employing metal chloride as cathode materials, which showed the potential to deliver high rate capability. Stimulated by AgCl as the cathode, it is possible to replace Ag with earth abundant metals with electrode modification. This concept provided a new view to develop Mg and other multivalent batteries such as Ca or Al.

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