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Toward the Design of High Voltage Magnesium-Lithium Hybrid Batteries using Dual-Salt Electrolytes

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We report a design of high voltage magnesium-lithium (Mg-Li) hybrid batteries through rational controls of the electrolyte chemistry, electrode materials and cell architectures. Prototype devices with a structure of Mg/LiFePO₄ and Mg/LiMn₂O₄ have been investigated. Mg/LiFePO₄ cell using a dual-salt electrolyte 0.2M [Mg₂Cl₂(DME)₄][AlCl₄]₂ and 1.0M LiTFSI exhibit voltages higher than 2.5 V (vs. Mg) and a high specific energy density of 246 Wh/kg under conditions that are amenable for practical applications. The successful demonstrations reported here could be a significant step forward for practical hybrid batteries.

The continuous increasing demands on the low cost, high density energy storage system and resolving of the grand environment challenges require battery designs that are beyond the scope of conventional lithium-ion batteries (LIB). Among the post LIB storage technologies, magnesium (Mg) batteries hold particular promises for reaching the high performance requirements due to its intrinsic safety, natural abundance and the high capacity of Mg metal.^{1, 2} When used as an anode, Mg metal has a low standard electrode potential (-2.37 V vs SHE) and fast deposition/stripping kinetics with nearly 100% reversibility without formation of dendritic structures.³ It also has much higher volumetric energy density (3832 mAh/cm³) than Li metal anode.⁴ Overall, Mg batteries have attracted considerable interests over the past years and substantial progresses, particularly on advanced electrolytes with improved stability and Mg ions transport mechanism within host materials, have been demonstrated.^{2, 5-7} The practical applications of Mg, however, are still facing great challenges, largely due to limited success on high voltage devices with Mg²⁺ ion intercalation.⁸⁻¹¹ By far, only the Chevrel

phase compounds show good Mg ions intercalation characteristics and stability.^{12, 13} Several recent attempts with new cathode materials (V₂O₅, WeS₂, TiS₂, graphene-like MoS₂, and MnO₂, MgCoSiO₄ etc.) show good promises for the future but substantial works are still required to fully understand and control the behavior.^{10, 14-18} These facts significantly restrict practical implementations of Mg metals for rechargeable batteries.

One of the viable strategies of utilizing Mg metals for rechargeable batteries is the design of hybrid systems, particularly through the use of well-established cathode materials from LIBs. This type of battery has a structure that has been outlined in several previous works, and has Mg metal anodes, Li-intercalation cathodes and dual salt electrolytes containing both Mg and Li ions.^{19, 20} Such a design is attractive because it has remarkable potentials of combining the advantages of Mg metal (safety and low cost) and Li⁺ intercalation cathode (fast kinetics and high voltage). In fact, this battery systems have been under intensive research over the past few years.²⁰ These works have documented devices with remarkable rate capability and cyclic stability but almost all of them are based on low voltage cathodes such as Mo₆S₈,^{19, 21, 22} TiS₂,^{23, 24} and Li₄Ti₅O₁₂.²⁵ The use of low voltage materials mitigate the challenges associated with Mg electrolytes, such as corrosion of current collectors and side reactions/ decomposition reactions at the electrode-electrolyte interface. Previous attempts with high voltage cathode materials, such as LiFePO₄, were mostly unsuccessful due to limited electrochemical window of electrolytes, poor control over the electrolyte-electrode interface and cell architecture design, which overall resulted in a very low Coulombic efficiency at high voltages.²⁰ More recently, attempt of applying solid state electrolyte (LISICON) to Mg/Li hybrid battery for mitigating problems listed above has been reported. However, the adopting LISICON to Mg-Li hybrid battery will bring a set of different technical problems associated with solid state electrolytes, which still face overwhelming technical challenges for the practical application.²⁶ Analogue to Mg-Li hybrid battery, Ichitsubo et

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al. has proposed “rocking-chair type” Mg-Li dual-salt battery concept and demonstrated at an elevated temperature of 150°C, where Mg²⁺ and Li⁺ ions can both act as charge carriers for the anode and cathode via Mg/Li alloy(anode) and Mg²⁺/Li⁺ co-intercalation (cathode).²⁷

In this paper we outline our approach on hybrid batteries with high voltage lithium ion cathode materials. This is based on a series of works we demonstrated recently, including the use of molybdenum metal (Mo) as the electrochemically stable current collector and dimagnesiumdichloro dimer complex cation (DMDC, Mg₂(μ-Cl)₂(DME)₄, DME=dimethoxyethane) based electrolytes.^{8, 28} The electrolytes with DMDC cation have remarkable activity and high stable voltage window (>3.4 V vs Mg) and bring exciting opportunities for the design of high voltage Mg based batteries.^{3, 28} In our experiment, we first examined the solvation behavior of a series lithium salts of LiAlCl₄, LiTFSI (TFSI = bis(trifluoromethane)sulfonimide), LiCl and LiPF₆ in 0.2M DMDC with a targeted Li⁺ ion concentration of 0.4 M. We found that while LiCl and LiPF₆ were not able to be dissolved completely, clear and transparent solutions were obtained with LiAlCl₄ and LiTFSI (Figure S1). Attempts with higher concentrations of LiAlCl₄ was unsuccessful, while LiTFSI had remarkable solubility (even with 2.0 M) in this particular electrolyte and was therefore used in this work because the electrolyte concentration is of a critical importance for hybrid batteries.

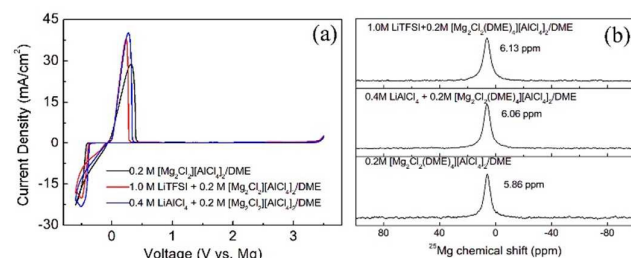


Figure 1(a) Cyclic voltammogram of Mg electrolyte and Mg-Li dual-salt electrolytes (with either 0.4M LiAlCl₄ or 1.0M LiTFSI) in DME solution. (b) ²⁵Mg NMR spectra of Mg electrolyte and Mg-Li dual-salt electrolytes. The addition of Li salts didn't affect the reversible deposition/stripping properties and the Mg chemical environment in the electrolytes.

The addition of LiAlCl₄ and LiTFSI to the Mg electrolyte did not change the electrochemical properties and the chemical properties of Mg ions. Figure 1a shows a set of cyclic voltammogram (CV) of electrolytes without and with Li salts, acquired with a three-electrode setup using a Pt (1mm in diameter) working electrode and two pieces of Mg strips as the reference and the counter electrode, respectively. All of these electrolytes have voltage windows of ~ 3.4V vs. Mg and the reversible deposition and stripping properties of Mg is not affected by addition of Li salts. In fact, the deposition overpotential is decreased slightly (around 20mV) after the addition of Li salts and the deposition current is increased. This observation is similar to the enhancement in the electroactivity that has been previously reported for Mg(BH₄)₂/LiBH₄ dual salt electrolytes.²² The efficiency is not affected and is all higher than 95%. We then studied the Mg

ions chemical binding properties with ²⁵Mg nuclear magnetic resonance (NMR, Figure 1b). The ²⁵Mg NMR spectra show that the ²⁵Mg chemical shifts for the DMDC, DMDC/LiAlCl₄, and DMDC/LiTFSI electrolytes are 5.85, 6.06, and 6.13 ppm, respectively. The similarity in chemical shifts suggests that the chemical environment of Mg²⁺ ions in these electrolytes are essentially the same, which has the characteristic bridged dichloride ligands between two Mg²⁺ ions as described in our

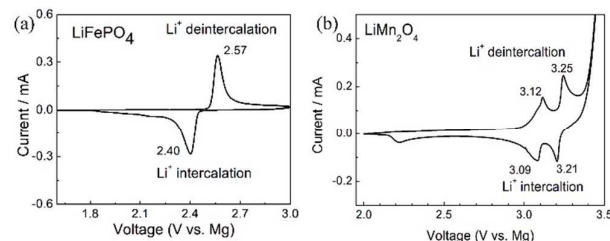


Figure 2 Cyclic voltammogram of (a) LiFePO₄ and (b) LiMn₂O₄ in the dual-salt electrolyte with 0.2M [Mg₂Cl₂(DME)₄][AlCl₄]₂ and 1.0M LiTFSI. The scan rate was 0.05 mV/s and two pieces of Mg strips were used for reference and counter electrodes, respectively.

previous paper.²⁸

The behaviors of the cathode materials LiFePO₄ and LiMn₂O₄ with cyclic voltammetry at 0.05 mV/s in the dual salt electrolytes with 0.2M DMDC and 1.0M LiTFSI are shown in Figure 2 (Figure 2a for LiFePO₄ and 2b for LiMn₂O₄). The CV for LiFePO₄ exhibited a set of well-defined redox peaks that is characteristic of Li ion intercalation.^{26, 29} The redox peak potentials are 2.57 V and 2.40 V for the anodic peak and cathodic peak, respectively, which are both expected given the standard potential difference of Li and Mg metals (Mg is 0.67V more positive).²⁶ In addition, it was observed that electrolyte was stable over the electrochemical operation window of LiFePO₄ with no obvious redox responses from the electrolyte. This agrees with results presented in Figure 1 and suggests such electrolytes are compatible with LiFePO₄ unlike the previously examined APC-based electrolytes.²⁰ In addition to LiFePO₄, we also examined the use of LiMn₂O₄ spinel cathode since it is more attractive because of its higher voltage. The CV profile of this material showed two set of redox peaks in the dual-salt electrolyte that are also characteristic for Li ion intercalation.³⁰ Even though the observation of reversible redox peaks is encouraging, further device tests with two electrodes returned with results that has poor Coulombic efficiency and low specific capacity due to the decomposition of electrolyte that is evident from the CV results in the sharp increases in anodic currents at voltages beyond 3.4V. Therefore, it is not further pursued in this work.

Prototype hybrid batteries with LiFePO₄ cathodes were assembled as Swagelok cells. The cathodes were prepared as thin, freestanding films using the rolling method and polytetrafluoroethylene (PTFE) as the binder. The active material loading was ~ 10 mg/cm² and typical active material loading for each electrode was ~ 8 mg. The cells were assembled using a stainless steel rod as the anode current collector and a molybdenum rod as the cathode current

collector (Figure 3a) because Mo metal is electrochemically stable over the entire stability window of the electrolyte (Figure S2). The use of these two rods ensures cells with proper sealing and electrochemical stability appropriate for testing high voltage cells designed in this work. In addition to this design, we also examined the use of graphite rod as the cathode current collector but cells often showed a fast capacity degradation due to the electrolyte evaporation problem. Typical battery testing data is presented in Figure 3b-d. Figure 3b shows a set of charge-discharge profiles for rates from 0.1C to 1.0C (1C=170 mA/g). The cell exhibited typical voltage profiles similar as those cycled in lithium cells (Figure S3). The electrode was able to deliver an outstanding capacity of ~ 140 mAh/g (respect to LiFePO₄) at a rate of 0.1C, > 80% of the theoretical capacity of LiFePO₄ (170 mAh/g). The observation of 20% loss in capacity can be due to extremely dense fixture of the freestanding electrode prepared by the rolling method and further improvements with electrode

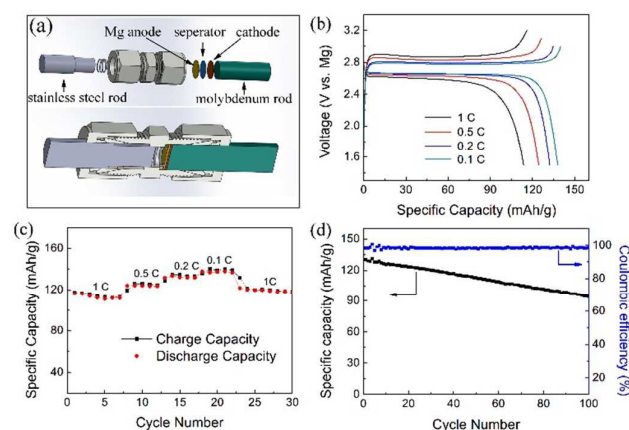


Figure 3 Assembly of prototype hybrid cells and testing results: (a) schematic illustration of the structure and assembly of the hybrid batteries with Swagelok-type cells, Mo rods, and Mg-Li dual-salt electrolytes consist of 0.2M [Mg₂Cl₂(DME)₄][AlCl₄]₂ and 1.0M LiTFSI; (b) typical charge-discharge profiles and (c) specific capacity (respects to the weight of LFP) at different rates; and (d) cyclic stability at 0.5C.

preparation might be able to improve the capacity remarkably. The repeated intercalation and extraction of Li ions was also confirmed with X-ray diffraction measurement (XRD) with the reversible formation of LiFePO₄ and FePO₄ (Figure S4). These data confirm the operation mechanism of the hybrid cells.

Figure 3c compares the specific capacities at different rates. The hybrid battery overall had remarkable rate performance considering the high active material loading of ~ 8 mg LiFeO₄ per electrode. The outstanding rate capability is believed to benefit from the high conductivity of the dual-salt electrolytes based on DMDC and the fast deposition/stripping of Mg on the anode side, and further demonstrated the advantage of Mg-Li hybrid batteries for high power application. Figure 3d shows the stability profile at a rate of 0.5C. The cell had high Coulombic efficiency and had gradual capacity decay along with cycles but overall was able to maintain a high capacity of more than 90 mAh/g after 100

cycles. A parallel test conducted in a pure lithium cell (Li/LFP) consisting of Li metal, LFP, and LiPF₆/EC-DMC electrolytes resulted a severe capacity decay (18 mAh/g remaining) after 100 cycles, as shown in Figure S5. The fast capacity degradation in Li/LFP is consistent with general understanding of rapid Li dendrite corrosion during the fast charge and discharge cycles.^{24, 31} In contrast to Li/LFP cells, Mg-Li/LFP hybrid cells deliver a much stable performance in terms of the

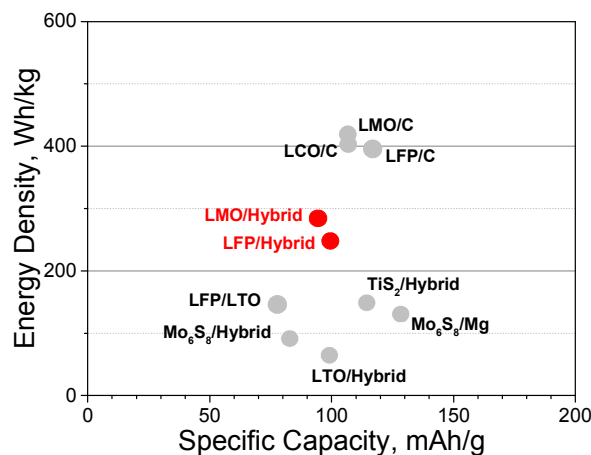
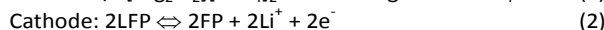
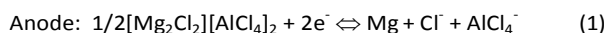


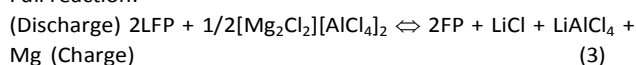
Figure 4 Specific energy density comparison for Mg (Mo₆S₈) battery, LIB (LMO/C, LCO/C, LFP/C), and Mg-Li hybrid batteries (LTO, Mo₆S₈, TiS₂, LFP, LMO as cathodes) without considering the mass of electrolytes.

capacity retention.

To calculate the specific energy density of Mg-Li hybrid system, it is important to reveal the full reaction equation for the charge and discharge processes. Without identifying the molecular formula of Mg²⁺ and Li⁺ species existing in Mg-Li dual-salt electrolyte, it is quite challenging to propose a meaningful reaction equation. Since the active Mg²⁺ specie presented in this work is identical to DMDC, the redox reactions of the charge and discharge can be given as follows:



Full reaction:



Based on the molecular weight of active materials at the discharge state (LFP and [Mg₂Cl₂][AlCl₄]₂), the specific energy density of Mg-Li hybrid battery demonstrated in this work (LFP) along with others lithium ion cathode materials are shown in Fig. 4. Detailed discussions about calculating the specific energy density of Mg-Li hybrid battery, such as considering the weight of electrolyte and lithium salts, can be found in the supporting information. Surprisingly, Mg-Li hybrid battery system using LFP (Mg-Li/LFP) as the cathode material can deliver a theoretical energy density up to 246 Wh/kg, which is quite higher than the energy density (134 Wh/kg) of the conventional pure Mg battery using Mo₆S₈ and the energy density (~ 143 Wh/kg) of LTO/LFP system. The higher energy

density of Mg-Li/LFP battery is benefited from the high output voltage (~2.5 V), which is significantly higher than 1.2 V of Mg/Mo₆S₈ battery and 1.9 V of LTO/LFP battery.

Conclusions

In summary, we demonstrate a high voltage and high energy density Mg-Li hybrid battery technology using Mg metal anode, LFP cathode (10 mg/cm²), and highly stable Mg-Li dual-salt electrolytes. Adopting Mo as a cathode current collector in the cell secures a stable electrochemical window of DMDC based electrolytes up to 3.4 V, thus allows the Mg-Li hybrid battery that could be paired with high voltage lithium cathodes, such as LFP and LMO. The reported cell architecture provides a conventional testing vessel for high voltage Mg batteries and Mg-Li hybrid batteries, where most metals suffer from corrosion problems caused by halide anions in electrolytes. In terms of battery performances, Mg-Li/LFP hybrid battery system demonstrates high energy density up to 246 Wh/kg, which is much higher than literature reported Mg-Li hybrid systems using relatively low voltage cathodes. In comparison to Li/LFP battery, Mg-Li/LFP battery demonstrates a superior cycling life and the battery safety own to its intrinsic feature – no dendrite formation on Mg anode. Notably, great potentials and challenges still need to be explored for Mg-Li hybrid battery system to become a practical battery. Extensive studies on electrochemical and chemical compatibilities of high voltage lithium cathode materials with Mg-Li hybrid electrolytes, reversible Mg deposition in Mg-Li hybrid electrolytes, and further optimization of cell architectures are on the way and are critical to continue to develop high performance Mg-Li hybrid battery systems.

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