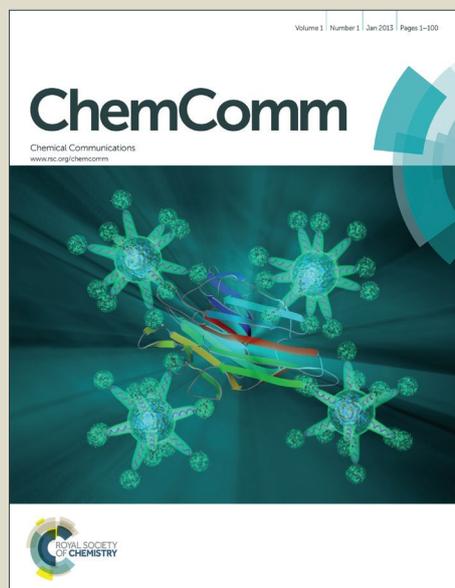


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## Toward the Design of High Voltage Magnesium-Lithium Hybrid Batteries using Dual-Salt Electrolytes

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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/LiFePO<sub>4</sub> and Mg/LiMn<sub>2</sub>O<sub>4</sub> have been investigated. Mg/LiFePO<sub>4</sub> cell using a dual-salt electrolyte 0.2M [Mg<sub>2</sub>Cl<sub>2</sub>(DME)<sub>4</sub>][AlCl<sub>4</sub>]<sub>2</sub> 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.<sup>1, 2</sup> 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.<sup>3</sup> It also has much higher volumetric energy density (3832 mAh/cm<sup>3</sup>) than Li metal anode.<sup>4</sup> 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.<sup>2, 5-7</sup> The practical applications of Mg, however, are still facing great challenges, largely due to limited success on high voltage devices with Mg<sup>2+</sup> ion intercalation.<sup>8-11</sup> By far, only the Chevrel

phase compounds show good Mg ions intercalation characteristics and stability.<sup>12, 13</sup> Several recent attempts with new cathode materials (V<sub>2</sub>O<sub>5</sub>, WeS<sub>2</sub>, TiS<sub>2</sub>, graphene-like MoS<sub>2</sub>, and MnO<sub>2</sub>, MgCoSiO<sub>4</sub> etc.) show good promises for the future but substantial works are still required to fully understand and control the behavior.<sup>10, 14-18</sup> 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.<sup>19, 20</sup> Such a design is attractive because it has remarkable potentials of combining the advantages of Mg metal (safety and low cost) and Li<sup>+</sup> intercalation cathode (fast kinetics and high voltage). In fact, this battery systems have been under intensive research over the past few years.<sup>20</sup> 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 Mo<sub>6</sub>S<sub>8</sub>,<sup>19, 21, 22</sup> TiS<sub>2</sub>,<sup>23, 24</sup> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.<sup>25</sup> 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 LiFePO<sub>4</sub>, 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.<sup>20</sup> 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.<sup>26</sup> 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 Mg<sup>2+</sup> and Li<sup>+</sup> ions can both act as charge carriers for the anode and cathode via Mg/Li alloy(anode) and Mg<sup>2+</sup>/Li<sup>+</sup> co-intercalation (cathode).<sup>27</sup>

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, Mg<sub>2</sub>(μ-Cl)<sub>2</sub>(DME)<sub>4</sub>, DME=dimethoxyethane) based electrolytes.<sup>8, 28</sup> 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.<sup>3, 28</sup> In our experiment, we first examined the solvation behavior of a series lithium salts of LiAlCl<sub>4</sub>, LiTFSI (TFSI = bis(trifluoromethane)sulfonimide), LiCl and LiPF<sub>6</sub> in 0.2M DMDC with a targeted Li<sup>+</sup> ion concentration of 0.4 M. We found that while LiCl and LiPF<sub>6</sub> were not able to be dissolved completely, clear and transparent solutions were obtained with LiAlCl<sub>4</sub> and LiTFSI (Figure S1). Attempts with higher concentrations of LiAlCl<sub>4</sub> 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.

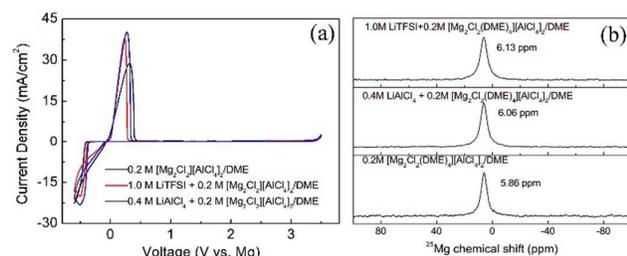


Figure 1(a) Cyclic voltammogram of Mg electrolyte and Mg-Li dual-salt electrolytes (with either 0.4M LiAlCl<sub>4</sub> or 1.0M LiTFSI) in DME solution. (b) <sup>25</sup>Mg NMR spectra of Mg electrolyte and Mg-Li dual-salt electrolytes. The addition of Li salts didn't affect the reversible deposition/stripping properties and the Mg chemical environment in the electrolytes.

The addition of LiAlCl<sub>4</sub> 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(BH<sub>4</sub>)<sub>2</sub>/LiBH<sub>4</sub> dual salt electrolytes.<sup>22</sup> The efficiency is not affected and is all higher than 95%. We then studied the Mg

ions chemical binding properties with <sup>25</sup>Mg nuclear magnetic resonance (NMR, Figure 1b). The <sup>25</sup>Mg NMR spectra show that the <sup>25</sup>Mg chemical shifts for the DMDC, DMDC/LiAlCl<sub>4</sub>, 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 Mg<sup>2+</sup> ions in these electrolytes are essentially the same, which has the characteristic bridged dichloride ligands between two Mg<sup>2+</sup> ions as described in our

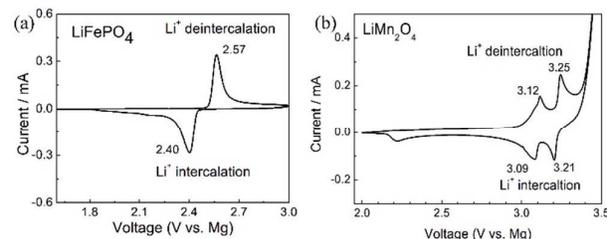


Figure 2 Cyclic voltammogram of (a) LiFePO<sub>4</sub> and (b) LiMn<sub>2</sub>O<sub>4</sub> in the dual-salt electrolyte with 0.2M [Mg<sub>2</sub>Cl<sub>2</sub>(DME)<sub>4</sub>][AlCl<sub>4</sub>]<sub>2</sub> and 1.0M LiTFSI. The scan rate was 0.05 mV/s and two pieces of Mg strips were used for reference and counter electrodes, respectively.

previous paper.<sup>28</sup>

The behaviors of the cathode materials LiFePO<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub> 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 LiFePO<sub>4</sub> and 2b for LiMn<sub>2</sub>O<sub>4</sub>). The CV for LiFePO<sub>4</sub> exhibited a set of well-defined redox peaks that is characteristic of Li ion intercalation.<sup>26, 29</sup> 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).<sup>26</sup> In addition, it was observed that electrolyte was stable over the electrochemical operation window of LiFePO<sub>4</sub> with no obvious redox responses from the electrolyte. This agrees with results presented in Figure 1 and suggests such electrolytes are compatible with LiFePO<sub>4</sub> unlike the previously examined APC-based electrolytes.<sup>20</sup> In addition to LiFePO<sub>4</sub>, we also examined the use of LiMn<sub>2</sub>O<sub>4</sub> 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.<sup>30</sup> 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 LiFePO<sub>4</sub> 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/cm<sup>2</sup> 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



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/Mo<sub>6</sub>S<sub>8</sub> 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/cm<sup>2</sup>), 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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