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Supplemental Information

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

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Experimental Section:

Materials and electrolyte synthesis: Magnesium dichloride ($MgCl_2$, 99.99%) and aluminum trichloride ($AlCl_3$, 99.99%) were purchased from Sigma Aldrich. Dimethoxyethane (DME) and LiTFSI were purchased from BASF. DME was dried over molecular sieve for > 48 hours prior to use. The electrolyte synthesis and preparation method was the same as described in our previous paper and was conducted inside an Ar-filled glove box. In a typical synthesis of 10 ml 0.2M $[Mg_2Cl_2(DME)_4][AlCl_4]_2$, $AlCl_3$ (0.53 g) was added to a suspension of $MgCl_2$ (0.38 g, in 10ml DME) in a 25 ml glass vial. The mixture was stirred at 60ºC using a sand bath for 6 hours, and was cooled to room temperature. A clear solution was obtained with no precipitation. The dual salt electrolyte was prepared by dissolving appropriate amount of Li salt in the above Mg electrolyte and was stirred overnight prior to use.

Materials measurement and characterization: the ^{25}Mg NMR spectra were obtained using a 600MHz Varian-Agilent spectrometer (Agilent, USA). The ^{25}Mg spectra were referenced to external 10.0M $MgCl_2$ in H_2O solution. All experiments were performed at ambient temperature.

Structure of electrodes were studied x-ray diffraction (XRD) using a Rigaku MiniFlex II instrument.

Electrochemical and battery tests: All electrolytes were aged at room temperature for at least 24 hours prior to testing. The CV tests were carried out inside an Ar-filled glove box at room temperature using a CHI660C potentiostat. The Mg deposition/stripping properties of each electrolyte were evaluated using cyclic votammetry and the three electrodes configuration. The working electrode was 1.0mm Pt (PEEK-encased) and was polished prior to each experiment. The reference and counter electrodes were pieces of freshly polished Mg metal strips.

Electrodes for prototype Mg batteries were prepared as freestanding thin films using the rolling method with PTFE (10 wt%), Super-P carbon (10 wt%) and 80 wt% active material. Typical active material loading was 10 mg/cm^2. The advantage of this electrode preparation method is that it doesn't need the use of metallic current collectors. Prototype batteries were assembled as Swagelok cells inside an Ar-filled glove box. A piece of Mg foil was used as the anode and the separator was glass fiber membrane. The anode current collector was stainless steel rod and the cathode current collector was molybdenum rods. About 60 μl of dual-salt electrolytes have been added to the Swagelok cells. Cells tests were performed on a Land battery tester (Wuhan Land Electronic Co.)

Capacity Calculation for Mg-Li hybrid battery system:

Full reaction for Mg-Li/LFP battery:

(Discharge) $2LFP + 1/2[Mg_2Cl_2][AlCl_4]_2 \Leftrightarrow 2FP + LiCl + LiAlCl_4 + Mg$ (Charge)

Specific capacity for Mg-Li/LFP = $2*26800/(2*LFP + Mg^{2+} + Cl^- + AlCl_4^-)$

= 2*26800/(2*157.76+24.31+35.45+168.79) = 98.52 mAh/g,

where molecular weights are 157.76 for LFP, 24.31 for Mg, 35.45 for Cl^-, and 168.79 for $AlCl_4^-$.

Specific energy density for Mg-Li/LFP = 2.5 V * 98.52 mAh/g = 246 mWh/g = 246 Wh/kg,

where 2.5V is an estimated output voltage for Mg-Li/LFP.

Specific energy density for Mg-Li/LMO = 3.1 V * 90.86 mAh/g=282 mWh/g = 282 Wh/kg,

where 3.1 V is an estimated output voltage for Mg-Li/LMO.

Specific energy density for LTO/LFP = 1.9 V * 75 mAh/g = 142.5 mWh/g = 143 Wh/kg, where 1.9 V is an averaged output voltage and 75 mAh/g is an estimated capacity for LTO/LFP battery system.

Energy densities of Mg-Li/LFP for different cases

	Mg-Li/LFP	w/ LiTFSI(1 M)*	w/ DME**
Energy density, Wh/kg	246	92	50

* In this work, Mg-Li/LFP batteries were assembled at the discharge state, which requires LFP and appropriate amount of Mg source ($[Mg_2Cl_2][AlCl_4]_2$) in the electrolyte to match the capacity of LFP. In that sense, the amount of lithium capacity is determined by LFP not LiTFSI in the electrolytes. However, certain amount of LiTFSI is necessary in the electrolyte to facilitate intercalation Li^+ ion to FP. If one include the mass of LiTFSI, calculated energy densities are 92, 134, and 171 Wh/kg, which correspond to the concentration of LiTFSI at 1, 0.5, and 0.25 M, respectively.

** Excessive amount of DME is only necessary for the case that has all Mg^{2+} ion resources in solution phase. If one considers to construct a Mg-Li/LFP battery with LFP, $[Mg_2Cl_2][AlCl_4]_2$ salts (not in solution phase) and appropriate amount of dual-salt electrolytes, the assembly of Mg-Li/LFP battery could be similar to conventional LIB or Mg cells without putting excessive electrolytes. In this case, the specific energy density of Mg-Li/LFP cell will be same as the number calculated without considering the mass of DME (246 Wh/kg).

Supplemental figures:

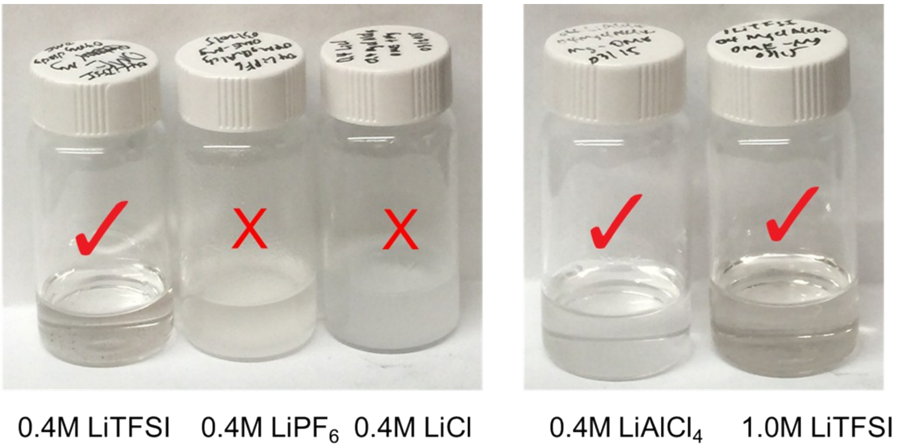

Figure S1: Photographs show solubility of Li salts in the Mg electrolytes. Clear and transparent Mg-Li dual salts electrolyte solutions were obtained with either 0.4M $LiAlCl_4$ or 1.0M LiTFSI.

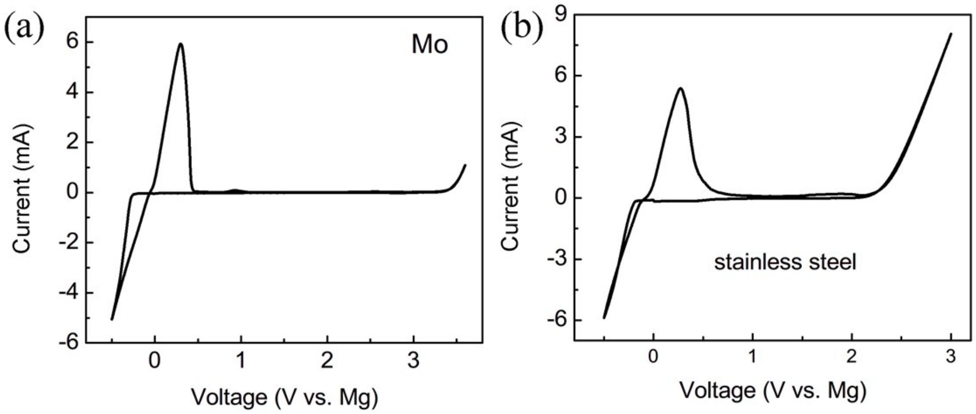

Figure S2: Cyclic voltammetry of (a) a piece of molybdenum foil and (b) a piece of stainless steel foil in 0.2M $[Mg_2Cl_2(DME)_4][AlCl_4]_2$ in DME. The data was acquired with three-electrode setup (two pieces of Mg strips as the reference and counter electrodes) and 20 mV/s. The results show Mo foil is electrochemically stable in the Mg electrolyte and has stability up to 3.5V.

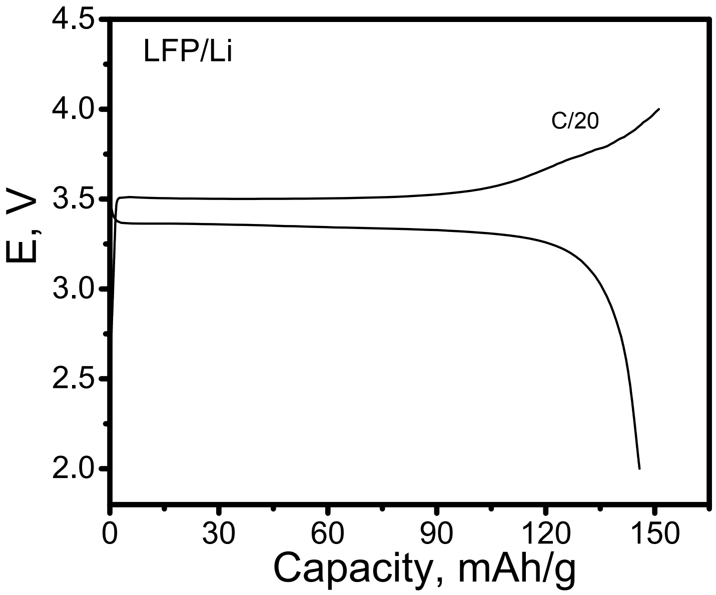

Figure S3 Typical charge-discharge voltage profiles for LFP/Li cell using $LiPF_6$/EC-DMC electrolytes at C/20.

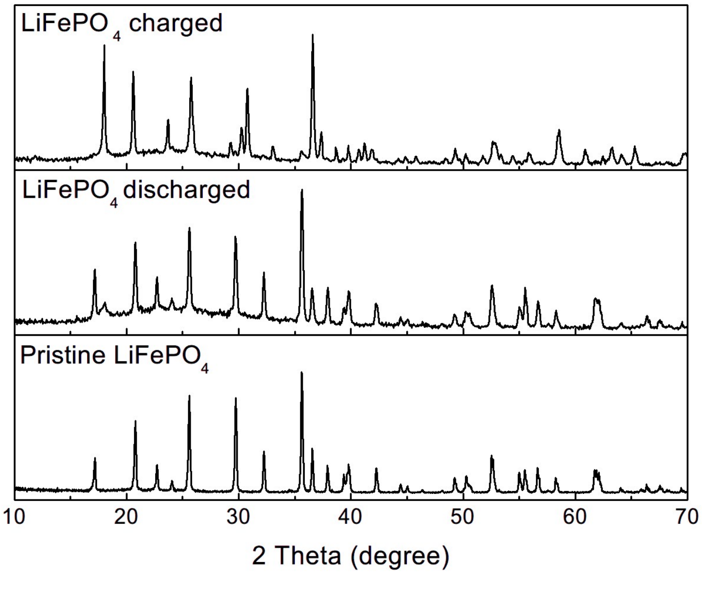

Figure S4: X-ray diffraction pattern of pristine $LiFePO_4$ and charged (de-lithiated) and discharged (lithiated) $LiFePO_4$ under battery conditions.

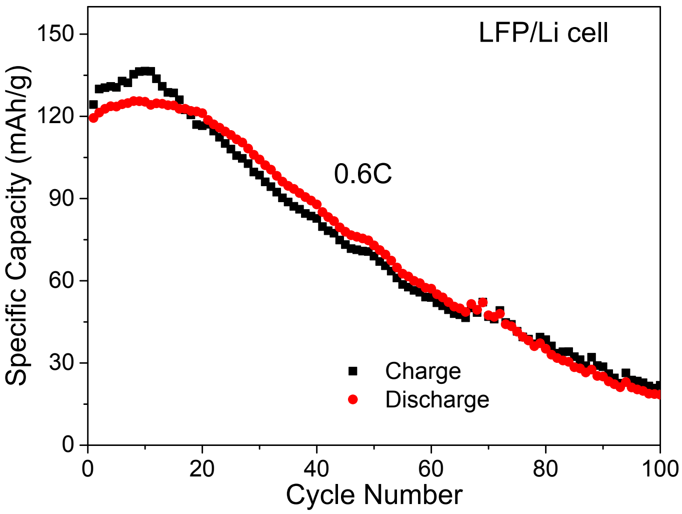

Figure S5: Capacity retention plots for LFP/Li cell using $LiPF_6$/EC-DMC electrolytes.