# **Electronic supporting information (ESI):**

Hybrid system for rechargeable magnesium battery with high energy density Zheng Chang, Yaqiong Yang, Xiaowei Wang, Minxia Li, Zhengwen Fu, Yuping Wu\*, Rudolf Holze

## 1. Physical characterization of the prepared LiFePO<sub>4</sub>.



Fig. S1. (a) SEM and (b) X-ray diffraction pattern of LiFePO<sub>4</sub>.

This 3D macroporous structure will facilitate the penetration of the aqueous electrolyte and give a large accessible surface area to enhance the exchange of  $\text{Li}^+$  between theaqueous electrolyte and the electrode. Moreover the XRD pattern of the 3D macroporous LiFePO<sub>4</sub> can be well indexed to the pure LiFePO4 phase with an orthorhombic structure (JCPDS card no. 83-2092)

### 2. Mg deposition/stripping Coulombic efficiency in PhMgBr and PhMgBr+LiBr electrolytes



**Fig. S2** Typical galvanostatic curves for Mg deposition-dissolution on Cu substrate in 1 M PhMgBr/THF (a), PhMgBr + LiBr/THF (b)

According to the ratio of the charge amount of magnesium dissolution to that of magnesium deposition shown in the above figure, Mg deposition/stripping Coulombic Efficiency in PhMgBr and PhMgBr+LiBr electrolyte are calculated to be 85.5% and 88.2%, respectively.

#### 3. The electrochemical window of the organic electrolyte



Fig. S3 The typical steady-state voltammograms of Cu electrode in the Grignard reagent PhMgBr of THF solution.

The electrochemical window of this electrolyte is 1.5 V. Above 1.5 V, it begins to decompose.

#### 4. Calculation of the energy density assembled Mg//LiFePO<sub>4</sub> battery

Mg: 2200 mAh g<sup>-1</sup> LiFePO<sub>4</sub>: 121.7 mAh g<sup>-1</sup> Discharge Potential: 2.12V The energy density is  $121.7 / (1+121.7/2200) \ge 2.12 = 245$  Wh kg<sup>-1</sup>.

## 5. The potential change of $Li^+$ ions in the LISICON film



**Fig. S4** Schematic illustration of the potential change of  $Li^+$  ions during the movement between the LiFePO<sub>4</sub> positive electrode in the aqueous electrolyte and the magnesium in the Grignard reagent-based electrolyte.

#### 6. Charge and discharge curves at different cycles for the rechargeable Mg battery



Fig. S5 The charge and discharge curves in the second, tenth, twentieth cycles for the rechargeable  $Mg/LiFePO_4$  battery.

7. Calculation of the energy density based on Mg and LiCoO<sub>2</sub> on the basis of the theoretic data Mg: 2200 mAh g<sup>-1</sup> LiCoO<sub>2</sub>: 145 mAh g<sup>-1</sup> Potential difference: 0.95 - (-2.37) = 3.32 V The energy density is 145 / (1+145/2200) x 3.32 = 451 Wh kg<sup>-1</sup>.