Supporting Information

High-Voltage Aqueous Magnesium-Ion Batteries

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Experimental Section

Synthesis of PPMDA@MCNTs composite

Pyromellitic dianhydride (PMDA) and ethylene diamine (EDA) were purchased from Sigma-Aldrich. The dispersible multiwall carbon nano-tube (MWCNT, diameter ~20 nm, length 5-30 µm) was obtained from Nanostructured & Amorphous Materials Inc.

Dispersible MWCNT (0.05 g) was first dispersed into 20 mL N-methyl pyrrolidinone (NMP) by ultrasonic for 30 min. PPMDA (0.872 g, 0.004 mol) was then added into solution and sonicated for another 10 min. The mixture was transferred into a flask. After EDA addition (0.268 mL, 0.004 mol) into the mixture, the reaction proceeded under refluxing and stirring for 8 h. The product was centrifuged, washed with NMP and ethanol for several times, dried at 100 ºC in air for 12 h, and finally heated at 330 ºC under argon for 8 h.

Synthesis of Li$_3$V$_2$(PO$_4$)$_3$@C

NH$_4$VO$_3$, NH$_4$H$_2$PO$_4$, LiOH and ascorbic acid were purchased from Sigma-Aldrich. The molar ratio of Li:V:P was 3.06:2.00:3.00. The NH$_4$VO$_3$, NH$_4$H$_2$PO$_4$, LiOH, 20 % excess ascorbic acid and glucose were add to the distilled water under vigorous stirring at 60ºC. The mixed solution was spray-dried to obtain the
precursor powders. Afterward, the precursor were first heated at 350°C for 4h and calcined at 700°C for 10h under Ar atmosphere.

**Preparation of Electrolytes**

Mg(TFSI)$_2$, AlCl$_3$, tetrahydrofuran (THF) and phenyl magnesium chloride were purchased from Sigma-Aldrich. Aqueous electrolyte was prepared by dissolve Mg(TFSI)$_2$ and MgSO$_4$ into the distilled water. Non-aqueous electrolyte solutions for rechargeable Mg batteries were based on reaction products of phenyl magnesium chloride (PhMgCl) Lewis base and AlCl$_3$ Lewis acid in tetrahydrofuran (THF).

**Materials Characterizations**

The morphology of the sample was investigated by scanning electron microscopy (SEM, Hitachi SU-70) and transmission electron microscopy (TEM, JEM 2100 FEG, 200 keV). All the samples for ex situ SEM were recovered from full aqueous Li-ion battery in three-electrode cell configuration after electrochemical cycling. The samples were washed by water three times and then dried under vacuum for two hours. X-ray diffraction (XRD) patterns were obtained on Bruker Smart 1000 (Bruker AXS, Inc.) using Cu Kα radiation with an airtight holder from Bruker.

**Electrochemical Measurements**

The electrodes were fabricated by compressing active materials, carbon black, and polytetrafluoroethylene (PTFE) at weight ratio of 8:1:1 onto the titanium grid. The
three-electrode devices for electrodes consist of $\text{Li}_3\text{V}_2(\text{PO}_4)_3@\text{C}$ (about 4mg) or PPMDA@MCNTs (about 4mg) as working, active carbon as the counter and Ag/AgCl as the reference electrodes. Cyclic voltammetry (CV) was carried out using CHI 600E electrochemical work station. The full AMIB cell was assembled in CR2032-type coin cell. The charge-discharge experiments were performed on a Land BT2000 battery test system (Wuhan, China) at room-temperature.
**Table S1.** The electrolyte stable window for several typical Mg-ion organic electrolyte.

| Electrolyte                                                                 | Stable Voltage Window |
|----------------------------------------------------------------------------|-----------------------|
| Grignard Solution(RMgX in ethers )                                         | ~1.3V                 |
| Mg Organoborate Moieties (Mg(BBu₂Ph₂)₂ in THF )                            | 1.9V                  |
| Magnesium haloalkyl aluminate complex (Mg(AlCl₂BuEt)₂)                     | ~2.2V                 |
| MgTFSI₂–MgCl₂ in DME                                                       | ~3.0V                 |

**Figure S1.** Transmission electron microscopy (TEM) image for the as-prepared LVP@C composite.
**Figure S2.** The pictures for a) the 4m Mg(TFSI)$_2$ electrolytes; b) the 4m Mg(TFSI)$_2$ with Li$_3$V$_2$(PO$_4$)$_4$ film for 24 hours; c) the electrode film after 24 hours’ immersion in the electrolyte.

**Figure S3.** The XRD patterns comparison for the LVP electrodes during first charge-discharge process and after the third discharge.
Figure S4. The magnified XRD patterns comparison for the LVP electrodes during first charge-discharge process and after the third discharge.

Figure S5. CV curves revolution for the LVP electrodes in the first ten cycles (a) and in the 10th to 20th cycles (b).
Figure S6. (a) Elemental mappings and (b) EDS patterns for the LVP electrode after 10 cycles.

Figure S7. The typical voltage profile of LVP in non-aqueous Mg-ion electrolyte at constant current of 0.2 C (20mA/g) using a two-electrode cell with Mg as the counter electrode.
Figure S8. Elemental mappings (a,b,c and d) and (e) EDS patterns for the PPMDA–MCNTs electrode at the discharged state after rinsing with water for 2 h.
**Figure S9.** Elemental mappings (a,b,c and d) and (e) EDS patterns for the as-prepared PPMDA@MCNTs after soaking into electrolyte and rinsing with water for 2h.

**Figure S10.** The typical voltage profile of PPMDA@MCNTs non-aqueous Mg-ion electrolyte at constant current of 0.2C (20mA/g) using a two-electrode cell with Mg as counter electrode.
Figure S11. Performances comparison for AMIB with other aqueous battery system based on various electrochemical couples. The cycling stability is color-coded with red, blue and green representing <100 cycles, 100~500 cycles, and >1000 cycles, respectively.