

---

## A high performance hybrid battery based on aluminum and LiFePO<sub>4</sub>

Xiao-Guang Sun,<sup>a\*</sup> Zhonghe Bi,<sup>a</sup> Hansan Liu,<sup>a</sup> Youxing Fang,<sup>a</sup> Craig Bridges,<sup>a</sup> M. Parans Paranthaman,<sup>a</sup> Sheng Dai,<sup>ab</sup> Gilbert M. Brown<sup>a</sup>

<sup>a</sup> Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

E-mail: sunx@ornl.gov; Fax: +1 865 576 5152; Tel: +1 865 241-8822

<sup>b</sup> Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

### Materials and Electrodes Preparation

LiFePO<sub>4</sub> was purchased from MTI Corporation. High purity aluminum foils and wires (99.999%, Sigma-Aldrich) were used as anodes and reference electrodes, respectively. Al foils were cut into disks with diameters of 1.2 cm to fit the electrochemical cells. These Al disks were mechanically polished using sandpaper, Nylon cloth with 5.0 μm alumina, and microcloth with 0.05 μm alumina (polishing kit, Pine Instrument), followed by activation in an acidic solution composed of 1 % HNO<sub>3</sub>, 65 % H<sub>3</sub>PO<sub>4</sub>, 5 % acetic acid and water for 5 min, and finally was rinsed thoroughly with deionized water and degreased in acetone for 5 min. Al wires were chemically polished. After cleaning with acetone and drying in air, they were taken inside the glove box (VAC, moisture <0.5ppm, oxygen <0.5ppm) in inert atmosphere for later use.

The cathodes were fabricated by a conventional coating method. A slurry consisting of LiFePO<sub>4</sub> (70 wt.%), Super-S carbon black (15 wt.%), and polytetrafluoroethylene (PTFE, 15 wt.%) in N-methyl-2-pyrrolidone (NMP) was uniformly spread onto E-Tek carbon cloth. Solvent was removed and the electrodes were cut into discs with diameter of 1.2 cm and further dried in a vacuum oven at 110 °C overnight. The active material loading was 1.0-3.0 mg/cm<sup>2</sup>.

1-ethyl-3-methylimidazolium chloride (EMImCl) was mixed aluminum trichloride (AlCl<sub>3</sub>) at a molar ratio of 1.1:1.0 inside an argon filled glove box to form acidic ionic liquid. 1.0 M Lithium tetrachloroaluminate (anhydrous, Sigma-Aldrich) was dissolved in the ionic liquid to form the electrolyte.

### Electrochemical Measurement and Battery Evaluation

Cyclic voltammetry was conducted in a BioLogic instrument. Coin cells were used to study the electrochemical behaviour of LiFePO<sub>4</sub> in the ionic liquid electrolyte with and without LiAlCl<sub>4</sub>. LiFePO<sub>4</sub> was used as working electrodes, and Al disk as both counter and reference electrode. The CVs were recorded at 0.1 mV/s between 0.5 V and 2.3 V vs. Al/Al<sup>3+</sup>. Aluminum deposition/stripping was evaluated using Pt as working electrode, aluminum coil and aluminum wire were used as counter and reference electrode, respectively.

Coin cells (CR2032) were used as prototype to evaluate Al-LiFePO<sub>4</sub> battery. Al disk was used as the anode, LiFePO<sub>4</sub>/C disk as the cathode, carbon fibre paper as the separator, and EMImCl-AlCl<sub>3</sub> (1-1.1) with and without 1.0 M LiAlCl<sub>4</sub> as the electrolyte. The cells were tested using an Arbin battery cycling instrument. The cells were charged and discharged under different current rates, based on the theoretical capacity of LiFePO<sub>4</sub> of 170 mAh g<sup>-1</sup>. The cut off voltages were 0.5 V and 2.2 V during discharge and charge, respectively.

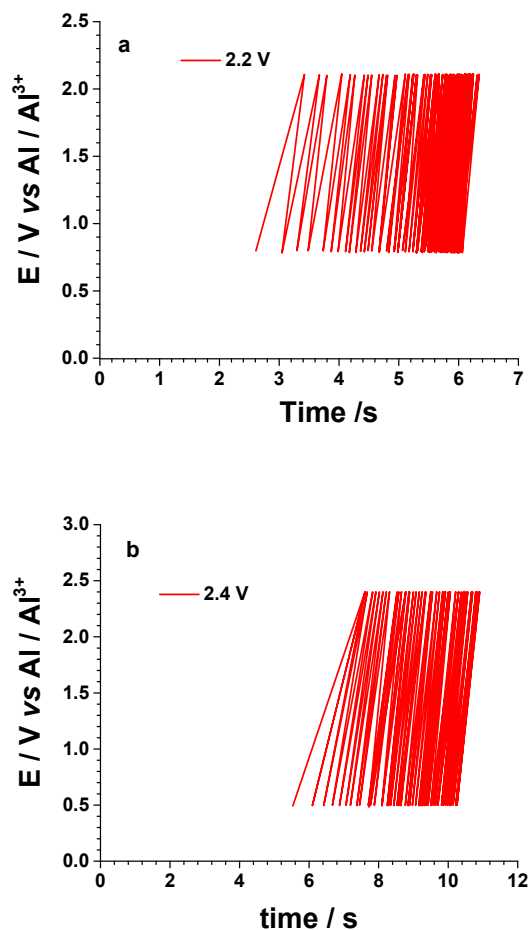


Fig. S1. Charge-discharge profile of Al||Carbon cloth cell in acidic ionic liquid with 1.0M LiAlCl<sub>4</sub> under a current of 50  $\mu$ A between a) 0.5 – 2.2V and b) 0.5 – 2.4 V.

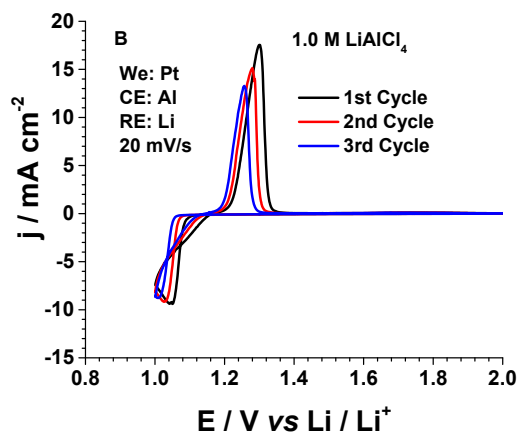
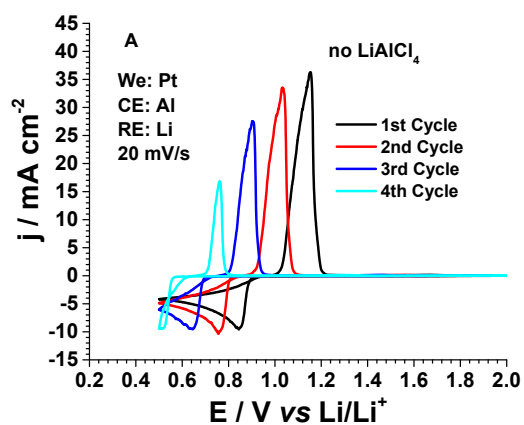


Fig. S2. Cyclic voltammetry of the acidic ionic liquid without (A) and with (B) 1.0M LiAlCl<sub>4</sub> on a Pt working electrode with Al as counter electrode and Li as reference electrode at a scan rate of 20 mV/s.

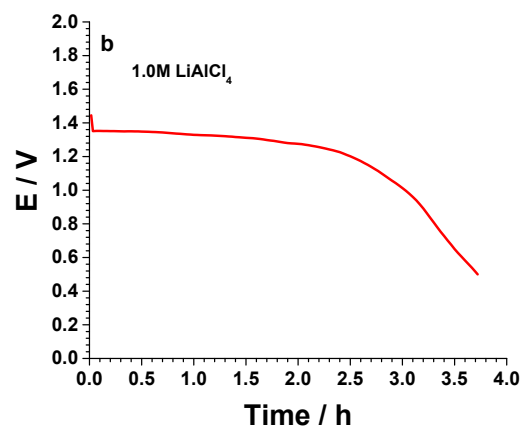
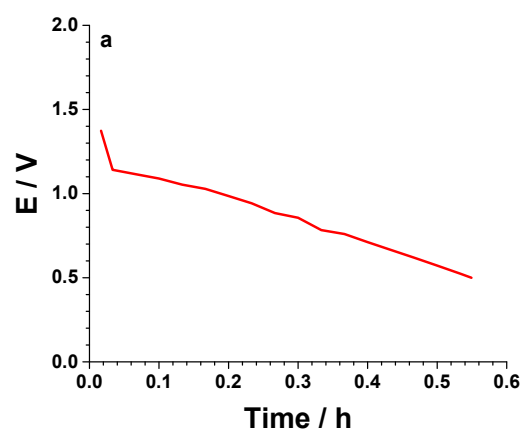


Fig. S3. Discharge profile of Al||FePO<sub>4</sub> batteries in a) EMImCl-AlCl<sub>3</sub> (1-1.1) and b) EMImCl-AlCl<sub>3</sub> (1-1.1) with 1.0 M LiAlCl<sub>4</sub> under a current of 50 $\mu$ A.

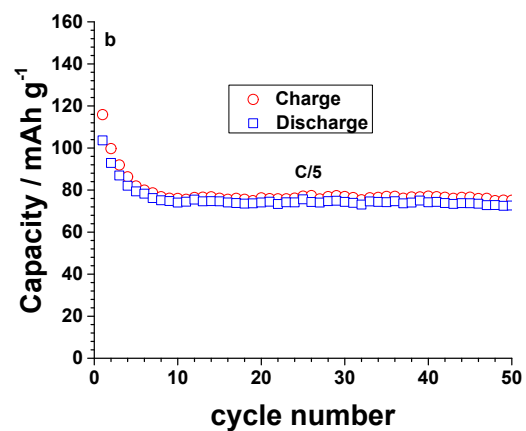
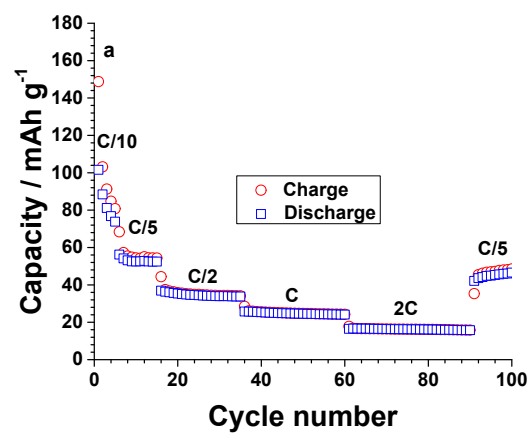


Fig. S4. a) Charge and discharge capacities and coulombic efficiencies of a hybrid battery in the EMImCl-AlCl<sub>3</sub> (1-1.1) electrolyte at different current rates; b) cycling performance of a hybrid battery using the same electrolyte at a current rate of C/5.