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A high performance hybrid battery based on aluminum anode and $LiFePO_4$ cathode

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A novel hybrid battery utilizing an aluminum anode, a $LiFePO_4$ cathode and an acidic ionic liquid electrolyte based on 1-ethyl-3-methylimidazolium chloride (EMImCl) and aluminum trichloride ($AlCl_3$) (EMImCl-$AlCl_3$, 1-1.1 in molar ratio) with or without $LiAlCl_4$ is proposed. The hybrid ion battery delivers an initial high capacity of 160 mAh g^{-1} at a current rate of C/5. It also shows good rate capability and cycling performance.

The environmental concerns over the use of fossil fuels and their limited resources, combined with energy security concerns, have spurred great interest in energy harvesting from renewable sources such as wind and solar.[1] However, both solar and wind are intermittent, and hence, in order to effectively utilize those renewable energies, low-cost electric energy storage (EES) devices are needed. Among various EES technologies, lithium ion batteries have been dominant in the electronic market ranging from small cellular phones to medium laptop computers and to large electric vehicles, and therefore, they are also good candidates for grid and stationary applications. However, one major issue is the high cost. As an alternative, cheap and naturally abundant elements based technologies such as sodium ion, magnesium ion and aluminum ion batteries have been intensively studied during the last few years.[2] Among these emerging technologies, aluminum batteries have distinct advantages because its three electron redox couple provides a high theoretical specific capacity of 2980 mAh g^{-1} and a high volumetric capacity of 8040 mAh cm^{-3}.

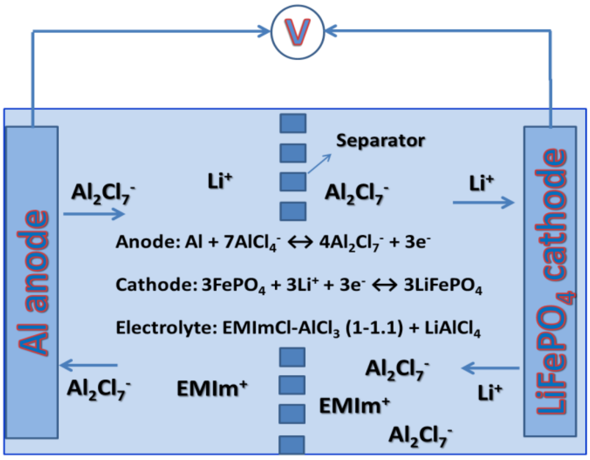

Fig. 1. Schematic illustration of the hybrid battery with Al as the anode, $LiFePO_4$ as the cathode and acidic ionic liquid as the electrolyte.

However, the development of rechargeable aluminum ion batteries faces major challenges from both electrolyte and cathode. Because of the low reduction potential of aluminum (-1.68 V vs. standard hydrogen electrode), aqueous electrolytes cannot be used as hydrogen will be generated before aluminum can be plated during the reduction process. So far, it has been shown that aluminum deposition/stripping is only possible in acidic ionic liquids based on mixtures of anhydrous $AlCl_3$ with organic halide salts such as EMImCl and N-(1-butyl)pyridinium chloride etc.[3] However, the strong acidic nature of the ionic liquids poses stringent requirement for the hardware of the aluminum batteries, as it was shown that corrosion was readily occurred to stainless steels.[4] Fortunately, there are some recent reports on the development of new electrolytes exhibiting reversible aluminum deposition/ stripping by replacing organic chloride salts with bis(trifluoromethanesulfonyl)imide (TFSI) based ionic liquids, neutral ligand based complexes, and organic solvents.[5] These alternative electrolytes hopefully can alleviate the corrosion problem to some extents. On the other hand, the challenge facing the aluminum cathodes results from its own advantage, i.e. trivalent cation, which makes its intercalation/de-intercalation very difficult.[6] Other challenges facing aluminum ion batteries are low cell voltage and poor cycling performance.[7] Recently, two groups led by Dai and Jiao et al reported good cycling performance on high voltage rechargeable aluminum ion batteries utilizing three-dimensional graphitic-foam and carbon paper as the cathode, respectively.[2i, 8] Besides aluminum ion batteries, Chang et al.

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Electronic Supplementary Information (ESI) available: [details of experiment and addition cycling data]. See DOI: 10.1039/x0xx00000x reported good cycling performance on an asymmetric capacitor based on Prussian blue and active carbon electrodes in an aqueous electrolyte.[9] However, the reported capacities for the aforementioned batteries and capacitors were low, i.e. below 100 mAh g^{-1}. Herein we report a new rechargeable battery based on the hybrid chemistries of aluminum anode and lithium intercalation cathode $LiFePO_4$, which exhibits high capacity, good rate capability and cycling performance.

Fig. 1 illustrates the principle of such a hybrid battery in an acidic ionic liquid electrolyte based on EMImCl and $AlCl_3$ (1-1.1 in molar ratio). Fig. 2a shows that the slightly acidic electrolyte still supports reversible aluminium deposition/stripping, which is the foundation for the operation of this hybrid battery. For this hybrid battery, the electrochemical redox reactions are reversible aluminum deposition/stripping at the anode and lithium intercalation/de-intercalation at the cathode during charge-discharge process. The overall cell reactions can be described as following:

Anode: $Al + 7LiAlCl_4 - 3e^- \leftrightarrow 4LiAl_2Cl_7 + 3Li^+$

Cathode: $3FePO_4 + 3Li^+ + 3e^- \leftrightarrow 3LiFePO_4$

Overall: $Al + 7LiAlCl_4 + 3FePO_4 \leftrightarrow 4LiAl_2Cl_7 + 3LiFePO_4$

Similar concept has been proposed by us several years ago using λ–MnO_2 as the cathode.[10] However, low capacity and poor cycling performance were observed, probably due to the acidic nature of the electrolyte causing corrosive side reaction with possible gradual dissolution of the cathode material. Since then, we have made several modifications to improve the cycling performance of this new hybrid battery. Firstly, to avoid corrosion of the current collector, E-Tek carbon cloth was used as the substrate on which the cathode slurry composed of 70 wt% $LiFePO_4$, 15 % Super P carbon (C45) and 15 wt% poly(tetrafluoroethylene) (PTFE) was evenly coated. After evaporating the solvent, the electrodes were cut into discs with a diameter of 1.2 cm and dried under vacuum at 110 °C for overnight before cell assembling. Secondly, an insulating shallow cup made of polyethylene was used to contain the cathode electrode and the acidic electrolyte soaked in a carbon fibre paper. The cup was designed to fit inside the coin cell sealing gasket. Thirdly, a thin platinum wire was used as a bridge between the cathode and the coin cell base. To avoid shorting the coin cell during cramping, the wire was wrapped with Celgard at the edge of the cup. Finally, a fixed amount of 80 μl electrolyte was used to assemble the coin cells. This amount of electrolyte was enough to wet the cathode and the separator but avoided flooding the cup.

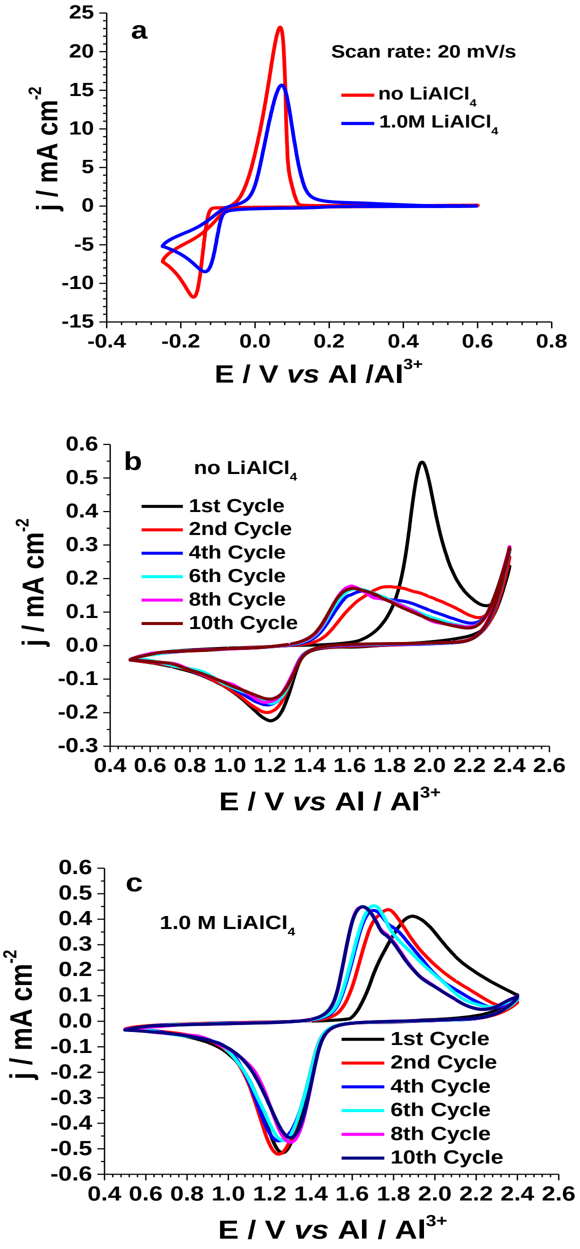

Fig. 2. a) Cyclic voltammetry of Pt working electrode in EMImCl-$AlCl_3$ (1-1.1) with and without 1.0 M $LiAlCl_4$ at a scan rate of 20 mV/s (aluminum coil and aluminum wire were used as counter and reference electrode, respectively). Cyclic voltammetry of Al||$LiFePO_4$ coin cell in b) EMImCl-$AlCl_3$ (1-1.1) and c) EMImCl-$AlCl_3$ with 1.0M $LiAlCl_4$ at a scan rate of 0.1 mV/s.

In principle, lithium salt is not needed in this new hybrid battery,[10] since the lithium ion extracted from the $LiFePO_4$ cathode during the charge process will sustain the necessary electrochemical reaction in the following cycles. To confirm this, a cyclic voltammetry was performed on an Al||$LiFePO_4$ coin cell using the pure acidic ionic liquid, EMImCl-$AlCl_3$ (1-1.1). Fig. 2b shows that indeed reversible redox peaks are observed, except that the first lithium de-intercalation peak at 1.97 V is well separated from the rest of the peaks. However, after the first cycle it is decreased to 1.80 V with lithium intercalation occurring at 1.18 V. To check whether the large peak separation is due to the lack of lithium salt in the electrolyte, 1.0 M $LiAlCl_4$ was added to the acidic ionic liquid electrolyte and CV was carried out under the same condition. Fig. 2a shows that the acidic electrolyte with 1.0 M $LiAlCl_4$ still supports reversible aluminium deposition/stripping except that slightly lower current density than that without the lithium salt is observed, probably due to the increased viscosity of the solution. Nonetheless, the CV in Fig. 2c clearly shows that with the presence of the lithium salt the overpotential of lithium de-intercalation is decreased to 1.89 V. After the first cycle reversible lithium intercalation/de-intercalation are observed at 1.3 and 1.7 V, respectively. The decreased lithium de-intercalation potential coupled with the increased intercalation potential for the one with lithium salt indicates that the presence of lithium salts improves the kinetics of the lithium reaction in the electrode. It is also noted in Fig. 2b and c that the current density with lithium salt almost doubles that without the lithium salt, which can translate into higher capacity for the former under the same current rate as shown later. Similar effect has been observed for a hybrid Mo_6S_8/Mg battery with all-phenyl complex (APC) and LiCl dissolved in THF as the electrolyte.[11] It is further noticed in Fig. 2b and c that there is an onset oxidation starting around 2.3 V. To avoid these side reactions, the cell voltage was cut off at 2.2 V during the charge process. It is also confirmed in Fig. S1 that there is almost no capacity contribution from the carbon cloth, no matter the charge voltage is cut off at 2.2 V or 2.4 V.

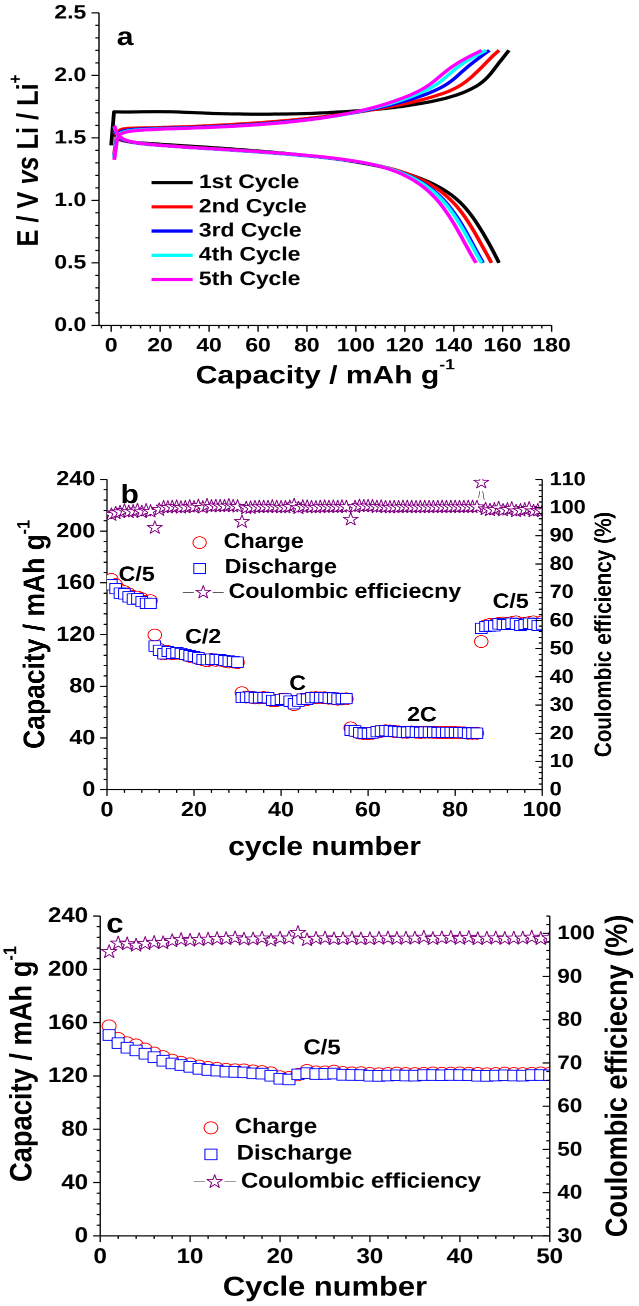

Fig. 3. a) Charge-discharge profile of a hybrid battery in the EMImCl-$AlCl_3$ (1-1.1) electrolyte containing 1 M $LiALCl_4$ under a current rate of C/5; b) charge and discharge capacities and coulombic efficiencies of the hybrid battery at different current rates; c) charge and discharge capacities and coulombic efficiencies of a hybrid battery using the same electrolyte at a current rate of C/5.

To further confirm whether the lithium intercalation is the major cathode reaction during the discharge process, Li||$LiFePO_4$ half-cells were assembled using Swagelok cells with 1.0 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethylene carbonate (DEC) (1/1/1 in volume) as the electrolyte. The cells were charged under a current of 50 μA until the cell voltage reached 4.0 V, after which they were held constant until the current was decreased to less than 5 μA. After delithiation, the electrodes were disassembled and washed inside the glovebox with DMC for three times before drying under vacuum. The dried $FePO_4$ electrodes were then used to assemble Al||$FePO_4$ cells. The cells were discharged under a constant current of 50 μA. As shown in Fig S2a and b that the cell without addition of $LiAlCl_4$ takes less than 0.6 hr to reach 0.5 V whereas the one with $LiAlCl_4$ takes 3.8 hrs to finish the discharge process. The well levelled cell voltage at 1.35 V for the latter reminds the typical discharge profile of $FePO_4$ electrode. The contrast of cell performance in Fig. S2 confirms that indeed Li^+ ion intercalation/de-intercalation is the main cathode reaction in the hybrid battery. However, it should be mentioned that the voltage observed for the hybrid battery is well below the theoretical value, that is, 3.5 – (3.05 - 1.68) = 2.13 V. Similarly, for the hybrid battery based on high voltage MnO_2, a voltage of 2.15 V was observed, which was also far below the theoretical value of 4.0 - (3.05 - 1.68) = 2.63 V.[10] The exact reasons for the observed low cell voltages are not known now, which might be closely related to the specific electrolyte system and deems investigation in the further studies.

Fig. 3a shows the typical charge-discharge profile of the first five cycles of a hybrid battery using the acidic ionic liquid electrolyte containing 1.0 M $LiAlCl_4$ at a current rate of C/5. The charge and discharge capacities are 162.6 and 158.5 mAh g^{-1} respectively, resulting in high coulombic efficiency of 97.5%. The flat charge/discharge profiles in the first cycle are typical behaviour of $LiFePO_4$ in traditional carbonate electrolytes, except that there is a 0.2 V difference between the charge and discharge process, as has been noticed in the CVs (Fig.2). The overpotential in the charge process decreases after the first cycle, indicating an initial activation process within the electrode. Fig. 3b shows the rate capability of the hybrid battery. The reversible capacity gradually decreases to 144.1 after 10 cycles under the current rate of C/5. When the current is increased to C/2, the charge and discharge capacities are decreased to 119.6 and 111.0 mAh g^{-1}, respectively, which are stabilized at 99 mAh g^{-1} after 20 cycles. When the current is further increased to C and 2C, the reversible capacities are decreased to 71 and 44 mAh g^{-1}, respectively. However, once the current rate is decreased to C/5, the reversible capacity is recovered to a high value of 127 mAh g^{-1}. Fig. 3c shows the cycling stability of another hybrid battery cycled under a current rate of C/5. Similarly, the reversible capacities decrease in the first few cycles and they are still as high as 122 mAh g^{-1} after 50 cycles. These above cycling data clearly demonstrate that the hybrid batteries based on aluminum and Li chemistry indeed work as expected. As a comparison, the hybrid batteries using pure acidic EMImCl-$AlCl_3$ electrolyte deliver lower capacities under similar current rates (Fig. S3). This result is consistent with the CV data presented in Fig. 2 and is also similar to the result of a hybrid Mo_6S_8/Mg battery without addition of LiCl. [11]

In summary, we have demonstrated that coupling aluminum and lithium chemistry in one device can deliver high capacity and good cycling performance. The safe nature and earth abundance of aluminum, coupled with the safety of ionic liquid electrolytes [12] make this new kind of hybrid battery very attractive for grid and stationary applications. The recent development of new ionic liquids electrolytes exhibiting reversible aluminum deposition/stripping offers new opportunity for rechargeable aluminum ion batteries, which yet needs to be confirmed in the future. [5c, 5d, 5f-i]

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