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The rechargeable aluminum-ion battery

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We report a novel aluminium-ion rechargeable battery comprised of an electrolyte containing AlCl_3 in the ionic liquid, 1-ethyl-3-methylimidazolium chloride, and a V_2O_5 nano-wire cathode against an aluminium metal anode. The battery delivered a discharge capacity of 305 mAh g^{-1} in the first cycle and 273 mAh g^{-1} after 20 cycles, with very stable electrochemical behaviour.

Since the early 1990s, lithium ion batteries based on a carbonaceous material such as graphite as the anode, a lithiated metal oxide (LiMO, *e.g.* LiCoO_2) cathode, and an aprotic liquid electrolyte have been the subjects of intense scientific and commercial interest for portable electronics applications. In recent years, the demand for secondary/rechargeable batteries with higher operating voltages, improved cycling stability, higher power densities, enhanced safety, and lower initial and life cycle costs has increased to meet new needs for smaller, lighter, more powerful electronic devices. Growing interest in hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEVs) designed to simultaneously reduce dependence on fossil fuel-derived energy and to lower the carbon footprint of humans compounds the current need for advanced, cost-effective electrical energy storage technologies.¹ Due to their high energy density and low self-discharge rate, Li-ion batteries are considered the most promising technology for meeting these demands for the foreseeable future.^{2–4}

Aluminium is the most abundant metal and the third most abundant element in the earth's crust. An aluminium-based redox couple, which involves three electron transfers during the electrochemical charge/discharge reactions, provides competitive storage capacity relative to the single-electron Li-ion battery.^{5–7} Additionally, because of its lower reactivity and easier handling, such an aluminium-ion (Al-ion) battery might offer significant cost savings and safety improvements over the Li-ion battery platform. Aluminium has consequently long attracted attention as an anode in the Al-air battery because of its high theoretical Ampere-hour capacity and overall specific energy.^{8–11} Although these values are reduced in a practical battery because of the inability to operate aluminium and the air cathode at their thermodynamic potentials, and because water is consumed in the discharge reaction, the practical energy density still exceeds that of most commercially

available rechargeable battery systems.¹² The inherent hydrogen generation of the aluminium anode in aqueous electrolytes introduces additional limitations, which have been met by designing the batteries as reserve systems with the electrolyte added just before use, or as mechanically rechargeable batteries with the aluminium anode replaced after each discharge. Even with these adjustments, reliable electrically rechargeable aluminium/air batteries are considered unfeasible using aqueous electrolytes, due to the high corrosion and hydrogen evolution of aluminium in the electrolyte, which leads to a sharp reduction of the anodic efficiency. Furthermore, several studies have shown that in aqueous media Al/air batteries an oxide film covers the surface of the aluminium anode, which decreases the anodic voltage and cell efficiency.¹³ The literature is replete with studies investigating the suitability of ionic liquid-based electrolytes for electrodeposition of aluminium.¹⁴ A battery technology exploiting an Al-ion conducting ionic liquid electrolyte has been recently reported to show some promise.¹⁵

Herein, we report on a novel Al-ion battery system using V_2O_5 nano-wires as the cathode against an aluminium metal anode in an ionic liquid (IL), 1-ethyl-3-methylimidazolium chloride, -based electrolyte.¹⁶ To the best of our knowledge, the Al-ion battery configuration reported in this communication is the first to offer evidence of stable electrochemical behaviour with extended cycle life. We attribute these features to the synergistic effect of a suitable electrolyte, V_2O_5 nano-wire cathode and Al anode. Specifically, a key requirement for achieving high energy density of an Al-ion battery is an electrolyte having good ionic conductivity for Al^{3+} , a wide electrochemical stability window in the presence of metallic aluminium, and which wets and permeates the pores of the metal oxide cathode. The aprotic electrolyte should also exhibit reversible electrochemical deposition and dissolution of aluminium.

Based on the aforementioned studies of electrodeposition of aluminium in room temperature ILs,¹⁴ AlCl_3 dissolved in 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) was used as the electrolyte in the current study to examine the operation of the Al-ion battery at room temperature (25 °C). This electrolyte possesses different degrees of Lewis acidity depending on the [EMIm]Cl : AlCl_3 ratio, which provides an additional degree of freedom in tuning its properties. During discharge the prevalent AlCl_4^- anion in the electrolyte will react with the Al anode to form Al_2Cl_7^- complex species, which reacts with the cathode to form an aluminium intercalated V_2O_5 discharge product. An acidic electrolyte composition with 1.1 : 1 molar

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Fig. 3 (a) Voltage vs. time (b) voltage vs. sp. capacity and (c) cycle life plot of Al-ion battery containing aluminium anode, V₂O₅ nano-wire cathode in ionic liquid under the potential window 2.5–0.02 V and at a constant current drain of 125 mA g⁻¹.

of the Al-ion battery was found to be 1.8 V. Fig. 3a displays the voltage vs. time plot of the Al-ion battery, wherein no change in the potential of the Al³⁺ insertion/extraction plateau was observed. Fig. 3b shows the voltage vs. capacity plot of the Al-ion battery which demonstrates a well defined and very stable Al³⁺ insertion plateau at ~0.55 V. In the first cycle, the battery exhibited an Al³⁺ ion insertion capacity of 305 mAh g⁻¹ against 273 mAh g⁻¹ at the end of 20 cycles. These values are somewhat lower than the theoretical capacity of V₂O₅ against the Al³⁺ ion, which is estimated to be 442 mAh g⁻¹ considering a simple three electron transfer reaction (Al + V₂O₅ ↔ AlV₂O₅). Fig. 3c shows the galvanostatic cycling performance of the Al-ion battery, which nicely shows a high degree of reversibility and good capacity retention. The coulombic efficiency of the cell is not as high as would be needed for long-term practical use in a secondary battery, but its stability is quite encouraging. Significant crystallography and voltammetry studies are underway to understand intercalation of aluminium into V₂O₅ and other layered oxides. These studies will help shed light on the effect of variables such as the cell current density and electrolyte formulation on the coulombic efficiency and practical specific energy achievable in the Al-ion battery. Indeed based on the specific capacities observed experimentally, one might conclude that only about 0.7 moles of Al³⁺ ions participate in the actual redox reaction. As in the case of Li-ion secondary batteries, we anticipate significant opportunities for nanoscale engineering and chemical design of the Al-ion battery cathode to increase the overall cell potential. Additionally, we anticipate as significant efforts to pioneer ionic liquid and

other Al-conducting electrolytes to enhance cell performance at high voltages and high current drains.

In conclusion, we report the first example of a functional Al-ion rechargeable battery. The battery uses V₂O₅ as the cathode against an aluminium metal anode in an ionic liquid-based electrolyte. When evaluated in galvanostatic cycling and cyclic voltammetry measurements, the battery displayed promising electrochemical features with stable cycling behaviour over 20 charge–discharge cycles. The theoretical energy density of the Al-ion battery with V₂O₅ as the cathode against aluminium metal as the anode was determined to be 240 Wh kg⁻¹, which is not enough to power very much. But considering the other attractive attributes of an aluminium based secondary battery platform, the energy density of this first Al-ion cell is enough to initiate a global search for new materials and cell designs which we anticipate will lead to rapid and sustained improvements.

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