The rechargeable aluminum-ion battery

N. Jayaprakash, S. K. Das and L. A. Archer*

Received 18th September 2011, Accepted 11th October 2011
DOI: 10.1039/c1cc15779e

We report a novel aluminum-ion rechargeable battery comprised of an electrolyte containing AlCl₃ in the ionic liquid, 1-ethyl-3-methylimidazolium chloride, and a V₂O₅ nano-wire cathode against an aluminum 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. LiCoO₂) 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

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.² The inherent hydrogen generation of the aluminum 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 aluminum anode replaced after each discharge. Even with these adjustments, reliable electrically rechargeable aluminum/air batteries are considered unfeasible using aqueous electrolytes, due to the high corrosion and hydrogen evolution of aluminum 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 aluminum anode, which decreases the anodic voltage and cell efficiency.³ The literature is replete with studies investigating the suitability of ionic liquid-based electrolytes for electrodoposition of aluminium.⁴ A battery technology exploiting an Al-ion conducting ionic liquid electrolyte has been recently reported to show some promise.⁵

Herein, we report on a novel Al-ion battery system using V₂O₅ nano-wires as the cathode against an aluminum metal anode in an ionic liquid (IL), 1-ethyl-3-methylimidazolium chloride, based electrolyte.⁶ 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, V₂O₅ 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 Al⁴⁺, a wide electrochemical stability window in the presence of metallic aluminum, and which wets and permeates the pores of the metal oxide cathode. The opposite electrolyte should also exhibit reversible electrochemical deposition and dissolution of aluminum.

Based on the aforementioned studies of electrodoposition of aluminum in room temperature ILs,⁴ AlCl₃ 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:AlCl₃ ratio, which provides an additional degree of freedom in tuning its properties. During discharge the prevalent AlCl₄⁻ anion in the electrolyte will react with the Al anode to form Al₃Cl₇⁻ complex species, which reacts with the cathode to form an aluminum intercalated V₂O₅ discharge product. An acidic electrolyte composition with 1.1:1 molar...
ratio of AlCl$_3$ to ([EMIm][Cl]) was found to yield effective electrochemical deposition and dissolution of aluminium and was therefore used for the study. To verify the role played by the AlCl$_3$-[EMIm][Cl] electrolyte, electrochemical investigation of the same battery system was also performed with an electrolyte containing aluminium trifluoromethanesulphonate (Al triflate) dissolved in a conventional aprotic liquid mixture PC/THF (1:1 v/v). In contrast to the AlCl$_3$-[EMIm][Cl] electrolyte system, no electrochemical activity was observed in the measured voltage range $-0.75$–$4.2$ V, underscoring the importance of the IL-based electrolyte.

The V$_2$O$_5$ nanowires used for the cathode were prepared by a hydrothermal method. In a typical synthesis, 0.364 g of commercial V$_2$O$_5$ powder (Sigma-Aldrich) and 30 ml of DI H$_2$O were mixed under vigorous magnetic stirring at room temperature, and then 5 ml 30% H$_2$O$_2$ (Sigma-Aldrich) was added to this mixed solution and kept continuously stirred for 30 min. Finally a transparent orange solution was obtained. The resultant solution was then transferred to a 40 ml glass lined stainless steel autoclave and heated at 205 $^\circ$C for 4 days. The product was washed with anhydrous ethanol and distilled water several times. Finally, it was dried at 100 $^\circ$C for 12 h and then annealed at 500 $^\circ$C for 4 h in air. The synthesized product was characterized by Transmission Electron Microscopy (TEM, Tecnai, T12, 120 kV), powder X-ray diffraction (Scintgent X-ray diffractometer with Cu K$_\alpha$ radiation), cyclic voltammetry (Solartron’s Cell Test model potentiostat under the scan rate of 0.2 mV s$^{-1}$), and galvanostatic electrochemical charge-discharge analysis (Maccor cycle life tester, under the potential window 2.5–0.02 V).

The V$_2$O$_5$ cathode slurry was made by mixing 85% of the synthesized V$_2$O$_5$ nano-wires, 7.5% super-p carbon and 7.5% of PVDF binder in NMP dispersant. Electrodes were produced by coating the slurry onto a 10 micron stainless steel current collector at 105 $^\circ$C for 1 h initially and at 100 $^\circ$C for 4 h in a vacuum oven. Since the acidic electrolyte used has the tendency to etch copper, stainless steel (301 type stainless steel, McMaster Carr, USA) was used as the current collector. The resulting slurry-coated stainless steel foil was roll-pressed and the electrode was reduced to the required dimensions with a punching machine. Preliminary cell tests were conducted on 2032 coin-type cells, which were fabricated in an argon-filled glove box (AlCl$_3$ is highly reactive), using 10 micron Al metal as the counter electrode and a Whatman glass microfiber separator. The electrolyte solution was 1:1:1 anhydrous AlCl$_3$ in 1-ethyl-3-methylimidazolium chloride.

The phase purity and degree of structural order of the synthesized V$_2$O$_5$ was studied using a powder X-ray diffraction (XRD) pattern shown in Fig. 1a. The XRD obtained is in good agreement with the standard JCPDS pattern (File No. 89-0612) and shows the existence of phase pure orthorhombic V$_2$O$_5$ with Pmmn space group. The absence of any undesirable peaks demonstrates the presence of a phase pure product and the miller indices (hk0) of all the characteristic peaks are marked as per the standard pattern. Fig. 1b and c shows the transmission electron microscopy (TEM) image of the as synthesized V$_2$O$_5$ nano-wires. It is apparent that the synthesis procedure yields uniform and nearly monodispersed nanostructures having uniform diameters throughout their entire length and sharp, well-defined surfaces.

To evaluate the feasibility of the electrolyte and the synthesized V$_2$O$_5$ nano-wires for Al-ion battery applications, electrochemical properties were examined by cyclic voltammetry and galvanostatic cycling analysis. Fig. 2a and b show the cyclic voltammograms of the V$_2$O$_5$ cathode against the Al metal anode in two different electrolytes: 1:1 v/v of Al triflate in PC/THF (Fig. 2a) and 1:1:1 molar ratio of AlCl$_3$ in ([EMIm][Cl]) (Fig. 2b) at room temperature. As mentioned earlier, no electrochemical activity was observed for the Al-ion battery using Al triflate in PC/THF as the electrolyte and V$_2$O$_5$ nano-wire cathode in the measured voltage range of $-0.75$–$4.2$ V. On the other hand, a pair of cathodic and anodic peaks were observed for the Al-ion battery with V$_2$O$_5$ nano-wire cathode and AlCl$_3$ in the [EMIm][Cl] electrolyte under the potential window of 2.5–0.02 V. The CV pattern shown in Fig. 2b exhibited a cathodic peak at $\sim$0.45 V and a corresponding anodic peak at $\sim$0.95 V, respectively, which may be attributed to the insertion/deinsertion of Al$^{3+}$ ions into and from the orthorhombic crystal lattice structure of V$_2$O$_5$ nano-wires. Virtually no change in the peak position or peak current value was observed in the cyclic voltammogram shown in Fig. 2b even after 20 scans, which substantiates the electrochemical stability of the battery. For this reason, AlCl$_3$ in [EMIm][Cl] was chosen as the electrolyte for discharge/charge studies.

To further evaluate the electrochemical properties of the designed Al-ion battery, a galvanostatic discharge/charge reaction was performed at the cell voltage of 2.5–0.02 V at a constant current drain of 125 mA g$^{-1}$. The open circuit voltage...
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 Al$^{3+}$ 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 Al$^{3+}$ insertion plateau at ~0.55 V. In the first cycle, the battery exhibited an Al$^{3+}$ 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 V$_2$O$_5$ against the Al$^{3+}$ ion, which is estimated to be 442 mAh g$^{-1}$ considering a simple three electron transfer reaction (Al + V$_2$O$_5$ ↔ AlV$_2$O$_5$). 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 V$_2$O$_5$ 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 Al$^{3+}$ 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 V$_2$O$_5$ 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 V$_2$O$_5$ 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.

This publication was based on work supported in part by the Energy Materials Center at Cornell, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences, under Award Number DE-SC0001086, and by Award No. KUS-C1-018-02, made by King Abdullah University of Science and Technology (KAUST). Facilities available through the Cornell Center for Materials Research (CCMR) were also used for this study.

Notes and references