An aluminium battery operating with an aqueous electrolyte

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# Abstract

Aluminium is an attractive active material for battery systems due to its abundance, low cost, a gravimetric energy density of 2.98 Ah g-1 (c.f. lithium 3.86 Ah g-1) and a volumetric energy density of 8.04 Ah cm-3 (c.f. lithium 2.06 Ah cm-3). An aqueous electrolyte-based aluminium-ion cell is described using TiO2 nanopowder as the negative electrode, CuHCF (copper-hexacyanoferrate) as the positive electrode and an electrolyte consisting of 1 mol dm-3 AlCl3 and 1 mol dm-3 KCl. Voltammetric and galvanostatic analysis have shown that the discharge voltage is circa 1.5 V. Both a single cell and 2-cell battery are demonstrated using 10 cm2 electrodes and 126 mg and 256 mg total active material for the 1-cell and 2-cell batteries respectively. The single cell exhibits an energy density of circa 15 mW h g-1 (combined positive and negative electrode masses) at a power density of 300 mW g-1 with energy efficiency remaining above 70 % for over 1750 cycles. Initial characterisation shows charge storage is due to the presence of Al3+. Cell capacity is circa 10 mA h g-1 and operates with a discharge voltage of circa 1.5 V (efficiency >80 % at 20C charge/discharge rate).

Key Words: aqueous aluminium ion battery

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# Introduction

The consumption of renewable energy, excluding hydropower, has grown almost exponentially over the past 20 years [1]. Most of this growth has come in the form of distributed solar PV and wind power which can cause a number of problems for electricity grids. For example, cloud cover can cause output from solar PV plants to be subject to large voltage and power fluctuations. This can be alleviated through use of low energy but high power, high cycle life and fast response energy storage systems [2]. Given suitable electrode materials, the high conductivity of aqueous electrolytes mean aqueous intercalation batteries may be capable of providing these characteristics in addition to being safe, non-toxic and potentially low-cost when compared to non-aqueous systems, such as ionic liquids. This communication reports on the construction and testing of a fully functional aqueous Alion cell. It should be noted that the majority of Al-ion research focusses on room temperature ionic liquid electrolyte systems (RTILs) theoretically allowing the utilisation of aluminium metals high capacity through reversible deposition [3-10]. The primary research aim becomes the identification of positive electrode materials that will not severely limit cell capacity. Table 1 provides an overview of RTIL based Al-ion systems reported in the literature to date. Cycle life varies from just 50 to 7500. Applied currents also vary considerable between reported electrodes, form 12 mA g-1 up to 5000 mA g-1. The majority of studies use AlCl3/EMICl (1-Ethyl-3-methylimidazolium chloride) or AlCl3/BMICl (1-Butyl-3-methylimidazloium chloride) as the electrolyte. Given a suitable positive electrode, a high capacity and energy density cell could be constructed. The best-performing cell to date, with a natural graphite positive electrode, has achieved a capacity of c.a. 100 mA h g-1 when cycled at 198 mA g-1. However, the expense and corrosiveness of RTILs are significant disadvantages of such a battery system.

**Table 1.** Comparing Al-ion cells utilising room temperature ionic liquid (RTIL) electrolytes.

**Paper Electrode and Specific Cyclability Coulombic Voltage range/**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| D.-Y Wang et al, ***Nat Comm***  ***8***, 2017 [9] | Natural graphite/Al.  AlCl3/EMICl | ~60mAh g-1 at 660mA g-1.  100mAh g-1 at 198mA g-1. | 6000 cycles | ~100% | 1. plateaus between   2.5-1.5V |
| S. Wang et al,  ***ACS Nano 11***,  2017 [23] | CuS-C composite/Al.  AlCl3/EMICl | ~100mAh g-1 at 20mA g-1. | 300 cycles | ~100% | Charged between  1.3-2.V. Limited discharge plateau  between 1.05 and  0.1V. |
| Angell et al,  ***PNAS 114***,  2016 [24] | Graphite/Al  metal.  AlCl3/urea | ~73mAh g-1 at  100mA g-1 | 180 cycles | 100-99% | 1. plateaus between   2.2-1.0V |
| Lin et al,  ***Nature 520***,  2015 [21] | Graphitic foam/Al metal.  AlCl3/EMICl | ~60mAh g-1 at  5000mA g-1 | 7500 cycles | >95% | Plateau between  2.5-1.5V |

**Electrolyte Capacity Efficiency profile**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Pyrolytic graphite/Al metal.  AlCl3/EMICl | ~65mAh g-1 at 66mA g-1 | Stable over 200 cycles | ~98% | Plateau between  2.25–2.0V |
| Sun et al,  ***Chem. Comms***  ***51***, 2015 [25] | Carbon paper/Al  foil.  Molybdenum  current collector.  AlCl3/EMICl | ~70mAh g-1 at 100mA g-1 | Good capacity retention over  100 cycles graphite layer spacing  increases by  ~38% | ~100% after 3rd cycle | Plateau between  1.8-1.4V under discharge |
| Wang et al, ***App. Mater.***  ***Interfaces 7***,  2015 [26] | V2O5 (binder free)/Al metal.  AlCl3/EMICl | 239mAh g-1 at  44.2mA g-1 | Decreases to ~180mAh g-1 after 5th cycle | - | Limited plateau between 0.7 and  0.5V |
| Geng et al,  ***Chem. Mater.***  ***27***, 2015 [27] | Mo6S8/Al metal. AlCl3/BMICl | 70mAh g-1 at 12mA g-1.  40mAh g-1 at  60mA g-1 | Stable from 3rd – 50th cycles | >100% | Two plateaus.  Dominant plateau between 0.55-0.5V |
| Hudak, ***J.***  ***Phys. Chem.***  ***118***, 2014 [28] | Conducting polymers/Al  metal. AlCl3/  EMICl | 70-45mAh g-1 at  20mA g-1  (polypyrrole)  90-70mAh g-1 at  16mA g-1  (polythiophene) | 15% fade up to 100 cycles.  Negligible fade from 50th 400th. | >91% columbic  (polypyrrole)  , >96%  (polythiophe ne) | 0.6-1.9V/No plateaus. |
|  |  |  |  |  |  |

The use of water as solvent for an aluminium salt has the potential to provide a cheap, inherently safe and more conductive electrolyte system compared to RTILs. Table 2 summarises the literature available for the aqueous aluminium ion battery. Only three electrode materials, anatase TiO2, copperhexacyanoferrate (CuHCF) and aerogel V2O5 have been shown to allow the reversible intercalation of Al3+ in aqueous electrolytes [11-16]. The most successful negative electrode was black-anatase TiO2, reported by He et al (He, Peng, Chu, Li, & Tong, 2014), that produced a high capacity of 270 mAh g1, in 1 mol dm-3 Al(NO3)3, although only 300 cycles were reported. CuHCF was shown by Liu et al to give a capacity of 41 mAh g-1 at 400 mA g-1 in 0.5 mol dm-3 Al2(SO4)3 (Liu, Pan, Li, & Gao, 2015). A capacity fade of 41% was measured over 1000 cycles. CuHCF has also been tested as a positive electrode for an Al-ion cell containing organic electrolyte but reversible capacity was low at 5-14 mA h g-1 [13]. However, CuHCF, along with a number of other hexacyanoferrates, have also been shown to function as positive electrodes in other aqueous electrolytes containing K+, Na+, Mg2+ or Zn2+ [1417]. Specific capacities of approximately 50-60 mA h g-1 are often reported. It should be noted that the capacities quoted regarding aqueous Al-ion cells are for individual electrode materials and not operational cells, where the positive and negative materials must be jointly considered. Furthermore, these studies have been limited to half-cell analysis and not operated in a battery configuration. In this paper, we discuss the electrochemical performance of a combined cell and a two-cell battery, demonstrating an operational system based on an aqueous electrolyte containing Al3+.

**Table 2** Comparing electrodes used in aqueous aluminium electrolytes.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Paper** | **Electrode and Electrolyte** | **Specific Capacity** | **Cyclability** | **Columbic**  **Efficiency**[[1]](#footnote-1) | **Voltage range/ profile** |
| Kazazi et al,  ***Solid state***  ***Ionics 300***,  2017 [18] | **Half-cell –** TiO2 nano-spheres.  1M AlCl3.  (0.785cm[[2]](#footnote-2)) | 180mAh g-1 at 50.25mA g-1. 105mAh g-1 at 2010 mA g-1. | ~6% fade over  30 cycles | ~90% from  50.25mA g-1  2010 mA g-1. | -0.3V - -1.2V vs Ag/AgCl. Discharge plateau at -0.95V - -0.9V. |
| Gonzalez et al,  ***RSC Advances***  ***6,*** 2015 [19] | **Half-cell -** V2O5  aerogel.  1M AlCl3.  (Swagelok-T) | 120mAh g-1 at 60mA g-1.  ~15mAh g-1 at  200mA g-1 | ~40% fade at  60mA g-1 and  ~25% fade at  200mA g-1 over 13 cycles | ~85% | -0.4V – 0.15V vs  MSE. Discharge plateau at -0.15V. |
| Liu et al, ***J.***  ***Mater. Chem.***  ***3***, 2015 [12] | **Half-cell –**  CuHCF. 0.5M  Al2(SO4)3.  (<2mg, 0.5cm2) | 41mAh g-1 at 400mA g-1 | 45% fade over  1000 cycles | ~100% | 1-0.2V. No plateau. |
| He et al, ***J.***  ***Mater. Chem.***  ***2***, 2014 [11] | **Half-cell** – TiO2 nano-leaves.  1M Al(NO3)3.  (9mg) | 271mAh g-1 at 50mA g-1.  141mAh g-1 at 2A g-1 | 8.4% fade after  300 cycles at 50mA/g | ~100% | 1.35-0.45V.  Discharge plateau at ~0.97V.2 |
| Y. Liu et al,  ***Electro. Acta***  ***143***, 2014 [20] | **Half-cell –** TiO2 nano-wire array.  0.5M Al2(SO4)3 | 75mAh/g at 4mA/cm2 | - | ~85% | 1.1-0.9V/  Discharge plateau just below 1V |
| Liu et al,  ***Energy and Environ.***  ***Science 5***,  2012 [21] | **Half-cell**. TiO2 nano-tube array  film.  1M AlCl3 | 75mAh g-1 at  4mA cm-2 | - | ~90% | 1.1-0.4V/  Discharge plateau between 1.1 -  ~0.8V |

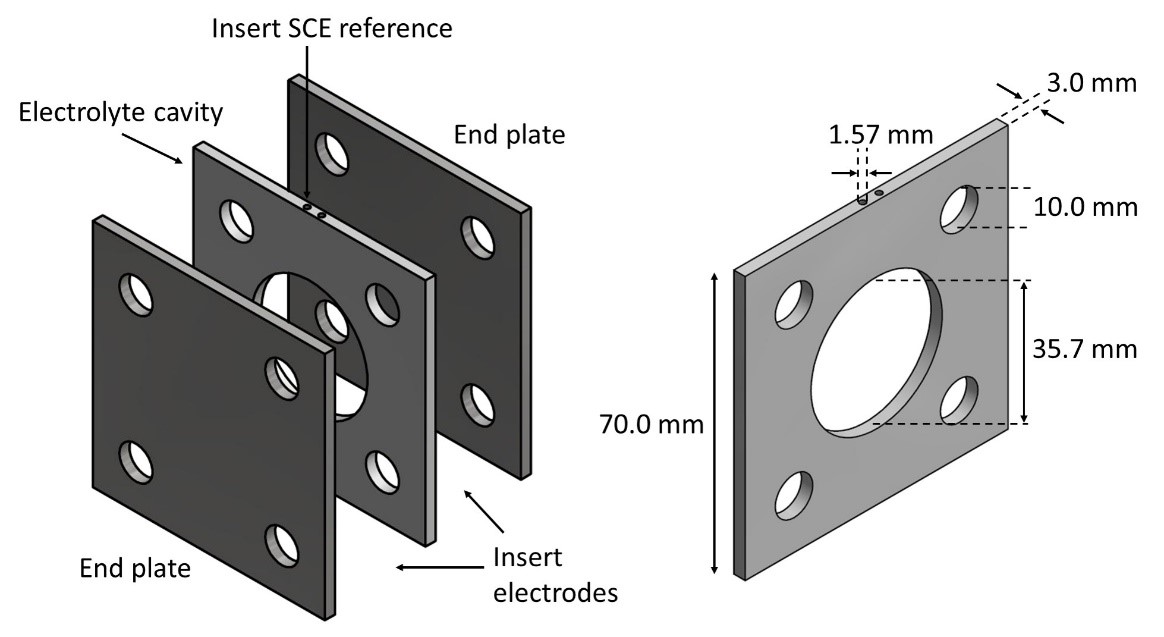
# Experimental procedure

Anatase-TiO2 nanopowder (< 25 nm) was used as received from Sigma Aldrich. Electrode inks were prepared through the addition of TiO2, carbon black (CB) and Nafion binder, in the ratio 9:0.5:0.5 by wt%. The positive electrode consisted of CuHCF, carbon black (CB) and Nafion binder in the ratio 8:1:1. Propanol was added to form inks of suitable viscosity (approximately 3:1 propanol:active material) and mixed at 5000 rpm for 30 minutes using Silverson shear blade mixer. The resulting inks were coated onto Sigracell PV10 carbon polymer current collectors from SGL and left to dry in ambient conditions.

CuHCF was prepared through a standard precipitation method. 1.5 mol dm-3 solution Cu(NO3)2 was added to 1 mol dm-3 solution of K3[Fe(CN)6] and stirred for a minimum of 2 hours at room temperature. The precipitate was centrifuged and washed five times before drying in air at 80°C and grinding to form CuHCF powder.

Standard 3-electrode glass cells were used for cyclic voltammetry (CV) to characterise the electrochemical activity of TiO2 in aqueous electrolytes. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire as the counter electrode. An Ivium multi-channel electrochemical analyser was used for CV scans. The galvanostatic performance of both electrodes was investigated in full cells through oversizing of the opposing electrode so that the cell capacity was only dictated by the electrode under investigation. An SCE reference electrode was used, in connection with a National Instruments data acquisition module, for voltage measurements of individual electrodes when being operated in a full cell, see figure 1. For these 2-electrode experiments, capacities of 16 mA h g-1 and 50 mA h g-1 were assumed for TiO2 and CuHCF respectively such that a 20C cycle rate corresponds to 333 mA g-1 for TiO2 and 1000 mA g-1 for CuHCF. A balanced cell, where the TiO2-electrode capacity was approximately equal to CuHCFelectrode capacity, used 10 cm2 of each active material on carbon polymer, separated by an electrolyte cavity, as shown in Figure 1. Positive and negative electrode loadings were 3.8 mg cm-2 and 8.5 mg cm-2 for the final cell, constituting larger format electrodes than previously reported. Electrode loadings for the 2-cell battery were 3.6 mg cm-2 and 9.2 mg cm-2. When operated as a unit cell, the positive electrode (CuHCF) acted as the working electrode for the Ivium analyser, with the negative electrode (TiO2) being connected to the counter and reference electrode terminals.

Neutron diffraction analysis was obtained using the GEM diffractometer via GEM Xpress operated at ISIS under project numbers (RN 1690193 & 1690194). Data sets were interpreted by the facility.

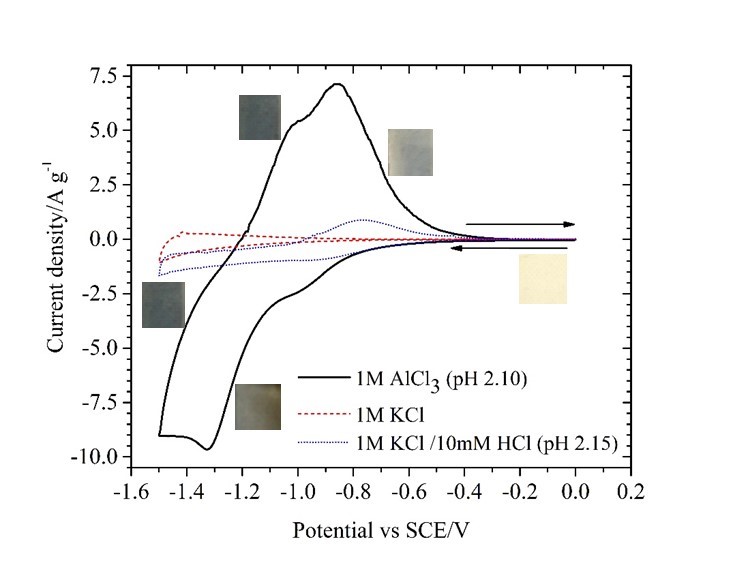


**Figure 1.** Schematic of the cell configuration used for the aqueous Al-ion cell. End plates were made of stainless steel and electrolyte cavity insert of PEEK.

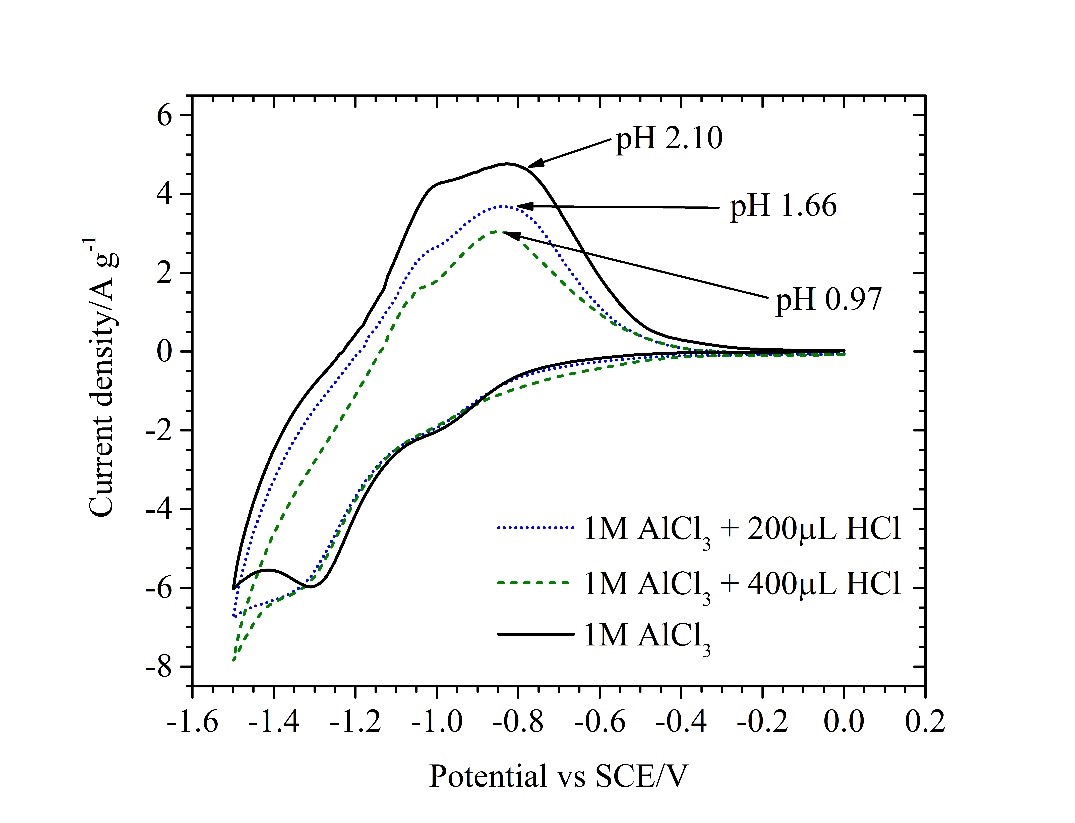
# Results and Discussion

A cyclic voltammogram was obtained at a TiO2 electrode (cell anode) in aqueous 1 mol dm-3 AlCl3, 1 mol dm-3 KCl and 1 mol dm-3 KCl/10 mmol dm-3 HCl. The potential was swept from 0 V to -1.5 V vs. SCE before returning to 0 V. A constant sweep rate of 10 mV s-1 was maintained throughout. Figure 2 presents the voltammogram with overlaying photographic images of the electrode surface at key potentials. Towards negative potentials, a reduction wave associated with Al3+ interacting with the TiO2 electrode commences at circa -0.8 V with an associated peak at circa -1.31 V. The current peaks at -9.7 A g-1. On the reverse sweep, an oxidation wave is observed, with a peak of 7.2 A g-1, at -0.85 V. Both reduction and oxidation waves have secondary peaks, at circa 0.98 V and circa -1.05 V respectively, indicating more than one reaction process associated with the TiO2/Al3+ interaction. In 1 mol dm-3 AlCl3, electrolyte stability at the electrode is good, with the onset of H2 evolution not yet visible at -1.5 V. An electrolyte containing 1 mol dm-3 KCl gave rise to no discernible redox activity, however, demonstrating that the redox phenomena are linked to the presence of Al3+ in the electrolyte solution. With the addition of HCl, small reduction and oxidation peaks, of approximately 1 A g-1, became apparent at roughly -0.9 V and -0.8 V respectively. This suggests an inherent response from anatase TiO2 in acidic aqueous electrolyte, which is an order of magnitude smaller in capacity than the response obtained in the presence of Al3+.

Photographic images were periodically taken, during a scan of a TiO2-only electrode, and have been overlaid at the appropriate potentials in Figure 2. These images graphically show the charge/discharge process at the negative electrode. In the charged state, the electrode is dark blue-grey, while in the discharged state the electrode almost returns to the original white colour associated with TiO2. These changes could be attributed to the reduction of Ti4+ to Ti3+ via four possible processes: Al3+ surface adsorption, Al3+ intercalation, H+ surface adsorption and/or H+ intercalation. Further mechanistic studies are planned to fully elucidate the processes involved.



**Figure 2.** Cyclic voltammetry of a TiO2 electrode in 1 mol dm-3 AlCl3 as well as ‘blank’ electrolytes consisting of 1 mol dm-3 KCl and 1 mol dm-3 KCl with 10 mmol dm-3 HCl. A scan rate of 10 mV s-1 was used.

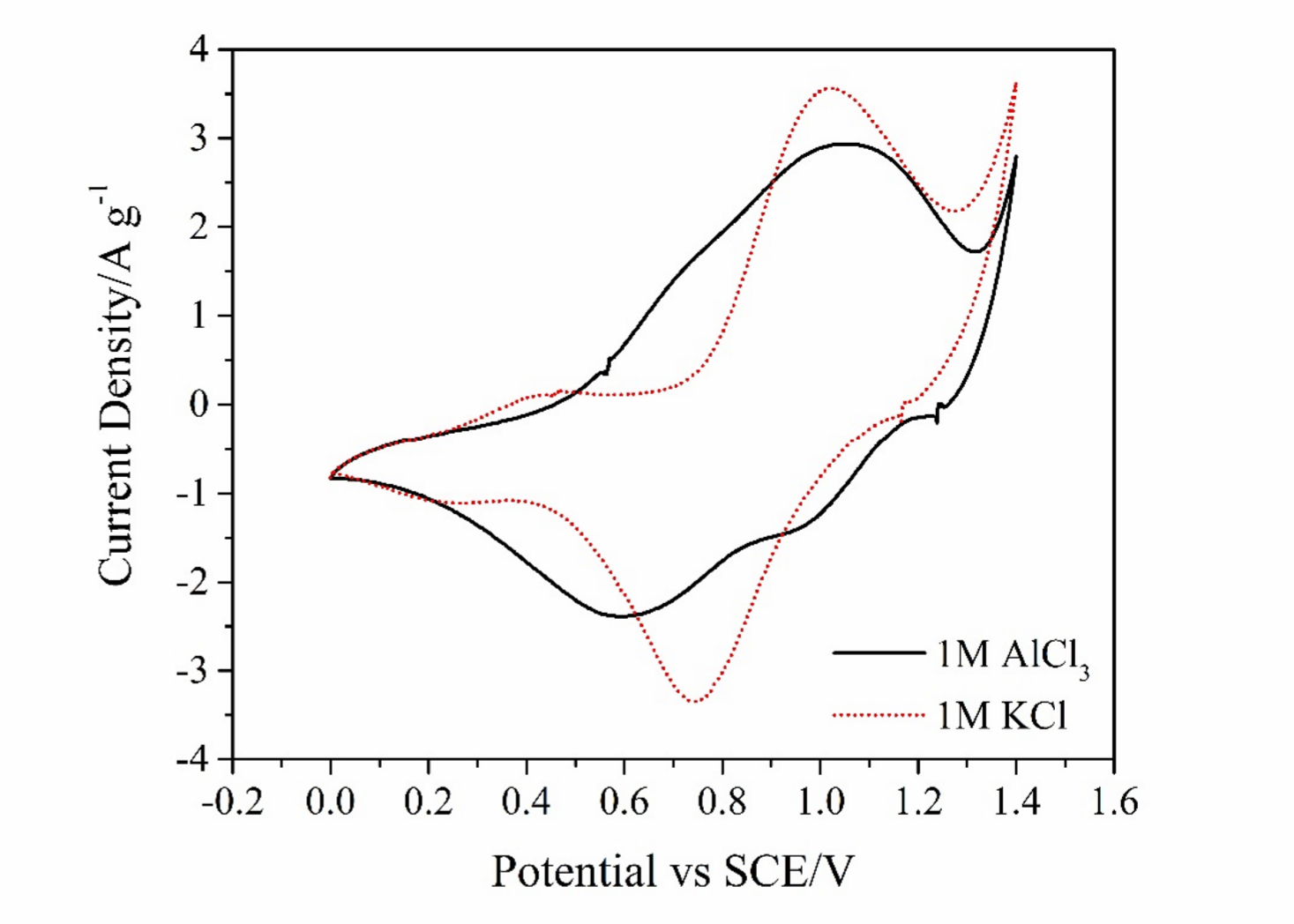


**Figure 3.** Cyclic voltammetry of a TiO2 electrode in 1 mol dm-3 AlCl3 electrolytes of increasing acidity. A scan rate of 10 mV s-1 was used.

The effect of acidity on the response is shown in Figure 3. Anodic peak currents are seen to decrease with increasing acidity, while cathodic peaks became decreasingly prominent, due to hydrogen evolution. This suggests that increasing the acidity of the electrolyte would be detrimental to cell performance. In conjunction with Figure 1, it can be concluded that the redox activity of anatase TiO2 is primarily due to the presence of Al3+ and not protons.

Neutron diffraction analysis of the negative electrode was carried out at ISIS using the General Materials Diffractometer (GEM). Two runs were undertaken: 79453 (freshly prepared electrode) and 79454 (electrode after charge/discharge cycling). The results showed a very good fit to a TiO2 structure with the two data sets having the following lattice parameters: 79453 a @ 3.7707(9), b @ 3.7706(10), c @ 9.4631(23) and 79454 a @ 3.7697(9), b @ 3.7695(10), c @ 9.4589(24). That is a difference of 0.001 Angstroms in a, 0.002 in b and 0.004 in c. This is a very slight shift in lattice parameters between an unused electrode and one that has been exposed to Al3+ in a battery environment. This represents a shift higher than the measured error (by an order of magnitude in a, by a factor of 2 in b and c) and so may be significant. While this lattice expansion may be evidence of Al3+ intercalation, further analysis is required on in-situ electrodes over a range of states of charge to validate the mechanism.

Cyclic voltammograms were obtained at CuHCF electrodes (cell cathode) in 1 mol dm-3 AlCl3 and 1 mol dm-3 KCl. The voltammetric response is presented in Figure 4. In 1 mol dm-3 AlCl3, broad reduction and oxidation peaks are visible at 0.6 V and 1.05 V respectively. Broad shoulders are also observed during the anodic and cathodic sweeps, centred on 0.7 V and 1.0 V respectively. Bulk oxygen evolution was observed at potentials more positive than 1.3 V vs. SCE. 1 mol dm-3 KCl produces sharper peaks at 0.74 V and 1.0 V, suggesting more facile insertion of K+ than Al3+. The use of a mixed Al3+/K+ electrolyte may therefore provide favourable cell operation where TiO2 and CuHCF are utilised as the negative and positive electrodes.



**Figure 4**. Cyclic voltammetry of CuHCF at 20 mV s-1 in 1 mol dm-3 AlCl3 and 1 mol dm-3 KCl. An SCE and Pt-wire were used as reference and counter electrodes.

With redox activity of TiO2 and CuHCF in Al3+ containing electrolyte confirmed, the performance of these electrodes was tested in aqueous Al-ion cells. Cells were limited by a single electrode by ensuring the capacity of the opposite electrode was considerably larger. TiO2 was galvanostatically charged to a specific capacity at a current density of 333 mA g -1. Figure 5 shows the discharge capacity and coulombic efficiency of TiO2 as a function of charge input. Above a 16-17 mA h g-1 charge input, there is limited increase in discharge capacity while the associated coulombic efficiency drops dramatically from >80% to <50% at beyond 30 mAh g-1. Both TiO2 and CuHCF limited 2electrode cells were then cycled at a charge and discharge current density of 333 mA g-1 for 1000 cycles. The results are summarised in Table 3. TiO2 produced a capacity of 14.5 mA h g-1 which decreased by ~7 % after 1000 cycles (c.f. 45 % capacity fade over 1000 cycles previously reported in the literature [13]) demonstrating that while the capacity is initially low, the electrode material and architecture is robust. The TiO2 electrode was cycled The capacity is considerably lower than would be expected from an intercalation electrode. The theoretical capacity of TiO2 is 335 mA h g-1

assuming intercalation proceeds according to reaction 1 [11], where 0<𝑥<1/3 since charge capacity is likely limited by the Ti4+/Ti3+ couple. This suggests Al3+ surface adsorption to be the most likely charge storage mechanism.

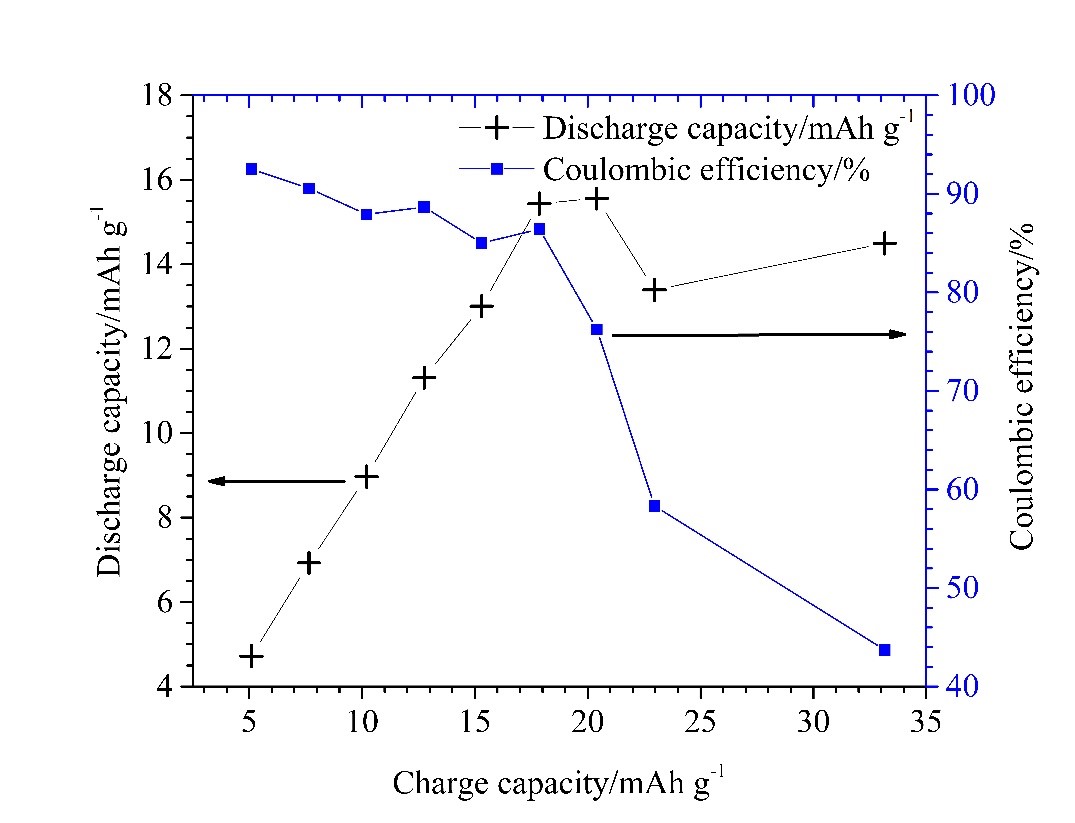
𝑇𝑖𝑂!+ 𝑥𝐴𝑙!!+3𝑥𝑒!↔ 𝐴𝑙!𝑇𝑖𝑂! *(1)*

The coulombic efficiency of TiO2 remained around 80% while the energy efficiency decreased by only 5% from a maximum of 71%. The more negative voltage profile in Figure 6 corresponds to the TiO2 electrode, vs SCE, during cycling. A very small initial voltage hysteresis shows the electrode should be capable of discharge at higher rates, however, coulombic efficiency is clearly low and may be indicative of a simultaneous self-discharge process.

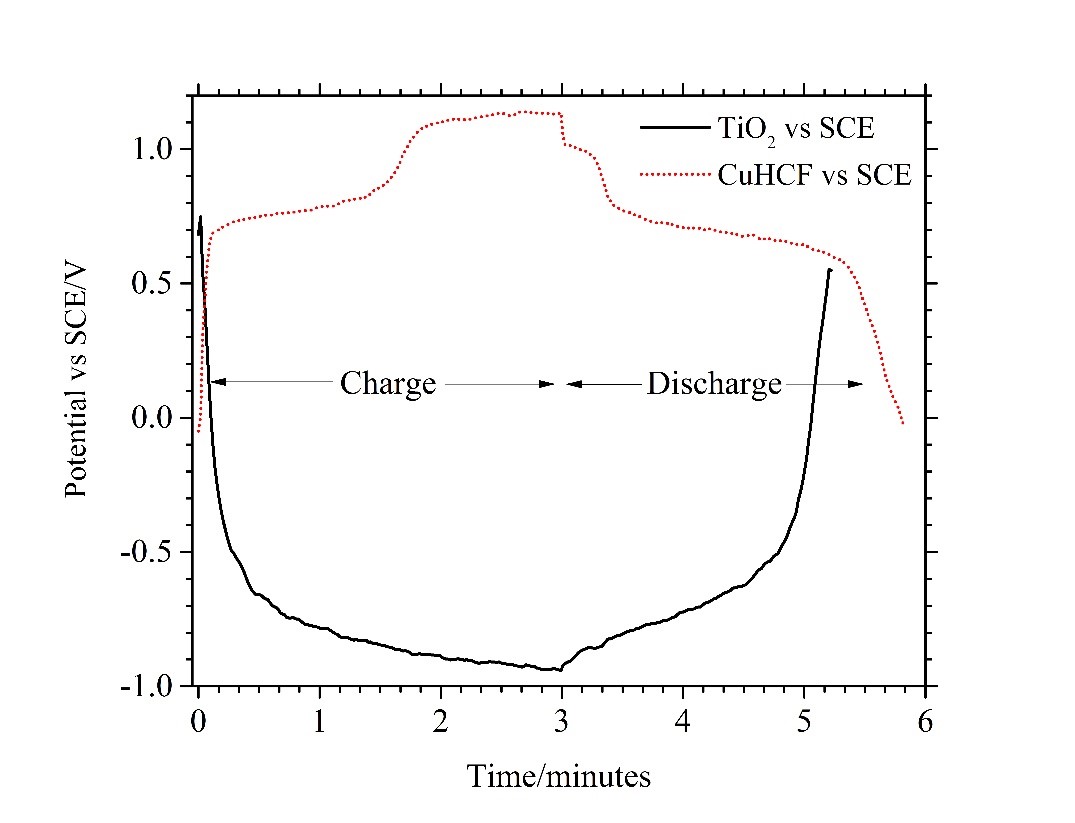
Galvanostatic cycling of CuHCF at 1000 mA g-1 produced a capacity of ~50 mAh g-1 throughout >1000 cycles. Coulombic efficiency was 97.2% after 20 cycles and decreased to 94%; energy efficiency of the CuHCF-limited cell remained at ~66% over >1000 cycles, which surpasses the previously reported cycling of electrodes incorporating CuHCF [5]. The more positive voltage profile in Figure 6 corresponds to CuHCF during a typical cycle. During charge, two plateaus are visible at 0.75 V and 1.1 V, each accounting for approximately half of the charge capacity. Similarly, two discharge plateaus are visible at 0.98 V and 0.65 V, although the first discharge plateau accounts for only 7% of the discharge capacity. The nature of the two plateaus is not yet understood. The 0.1 V hysteresis between final charge voltage and initial discharge voltage suggests the rate capability of CuHCF may be inferior to TiO2, although coulombic efficiency is clearly superior. The <100% efficiency is attributed to side reactions such as O2 evolution.

**Table 3.** Summary of performance of TiO2- and CuHCF- limited cells cycled in 1 mol dm-3 AlCl3 and 1 mol dm-3 KCl at a current density of 333 mA g-1 (based on the mass of the limiting electrode).

|  |  |  |
| --- | --- | --- |
|  | **TiO2 (333 mA g-1)** | **CuHCF (1000 mA g-1)** |
| **Capacity** | 14 mA h g-1 | 50 mA h g-1 |
| **Average discharge voltage** | -0.65 V vs SCE | 0.70 V vs SCE |
| **Coulombic efficiency** | 84-80% | 92-94% |
| **Energy efficiency** | 72-66% | 66% |
| **Cycled to** | >1000 | >1000 |

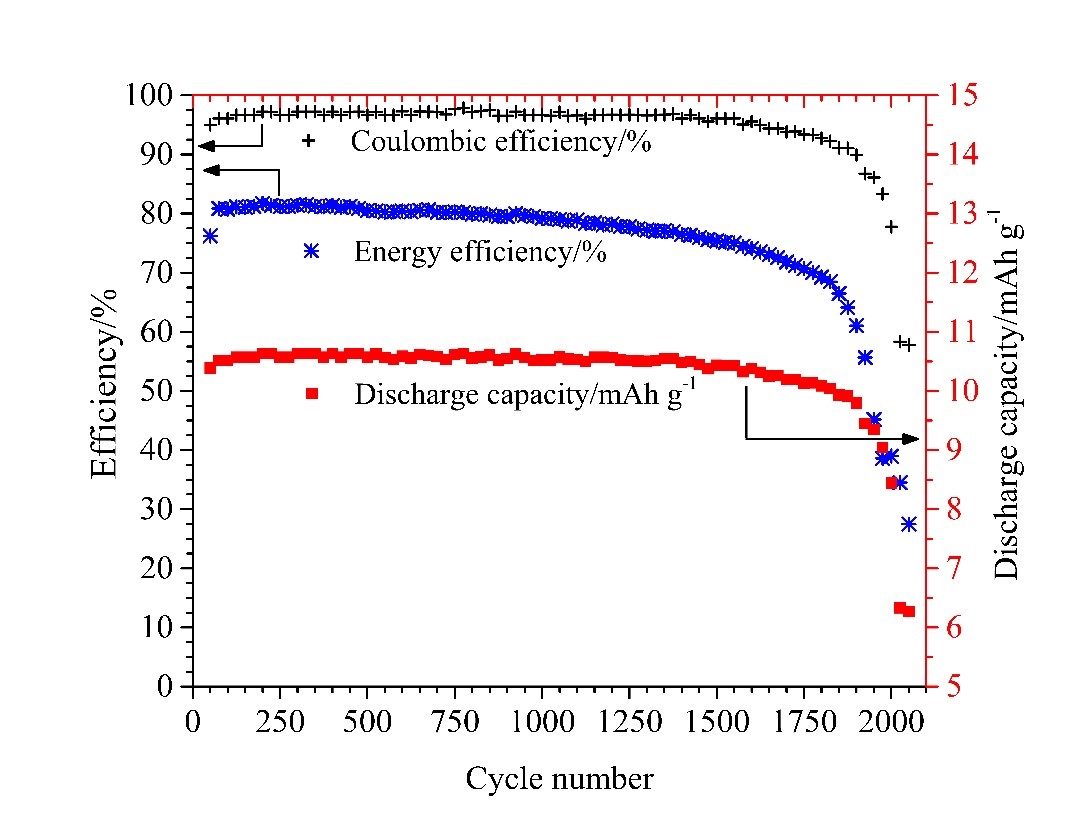


**Figure 5.** The discharge capacity and coulombic efficiency of a TiO2 electrode as a function of charge capacity when cycled at 333 mA g -1 in 1 mol dm-3 AlCl3/1 mol dm-3 KCl.

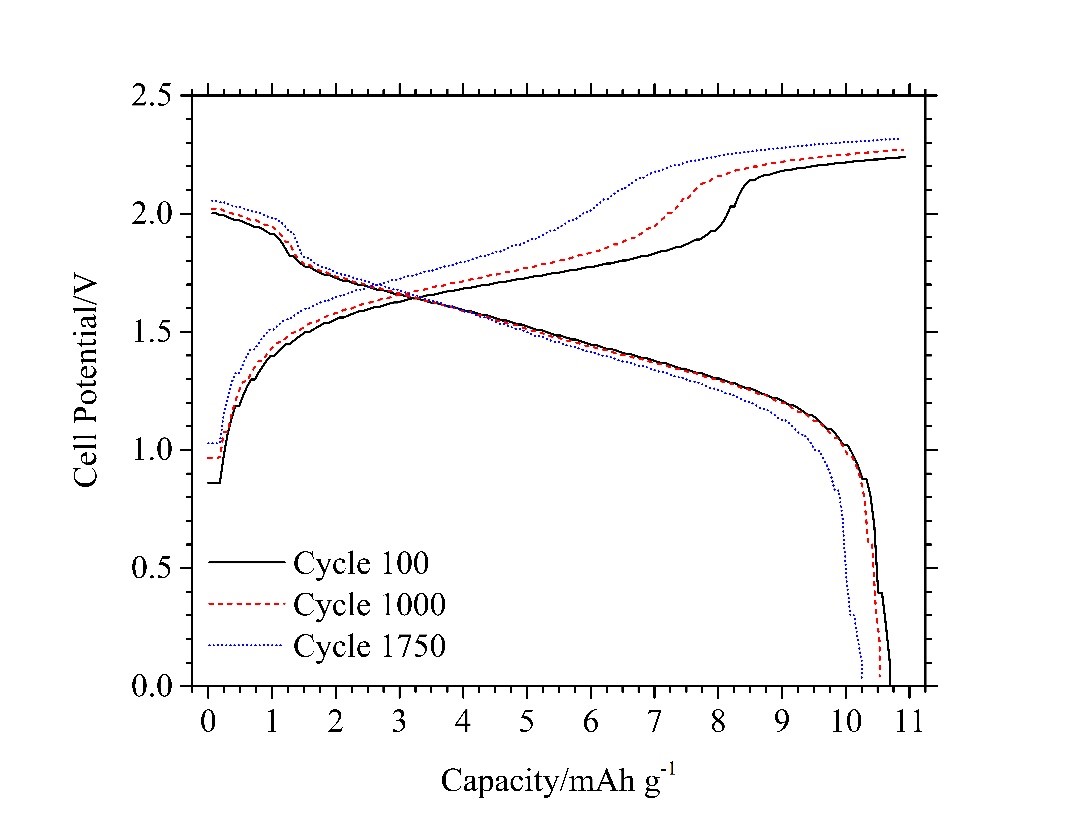


**Figure 6.** *Top (red-dotted)*: typical voltage profile, vs SCE, of a CuHCF electrode under cycling at 1000 mA g-1. *Bottom (black-solid)*: typical voltage profile, vs SCE, of a TiO2 electrode under cycling at 333 mA g-1. A 1 mol dm-3 AlCl3/1 mol dm-3 KCl electrolyte was used in both cells.

A balanced cell (85 mg TiO2 vs 38 mg CuHCF), was cycled nearly 2000 times at a current corresponding to a 20C rate. The efficiencies and discharge capacity throughout cycling is shown in figure 7 with the evolution of the voltage profile given in figure 8. A maximum capacity, calculated from the combined mass of electrodes, of circa 10.6 mA h g-1 remained above 10 mA h g-1 until the 1814th cycle. An average discharge voltage which ranged between 1.49 V at cycle 100 and 1.46 V at cycle 1750, gives the cell an energy density of ca. 15 mW h g-1. An initial coulombic efficiency of 96% was still above 90% by the 1900th cycle; energy efficiency decreased from ~80% to 70% at cycle number 1778. Therefore, while capacity and energy density remain low, a cell with good voltage, cycle life, efficiency and rate capability has been demonstrated.

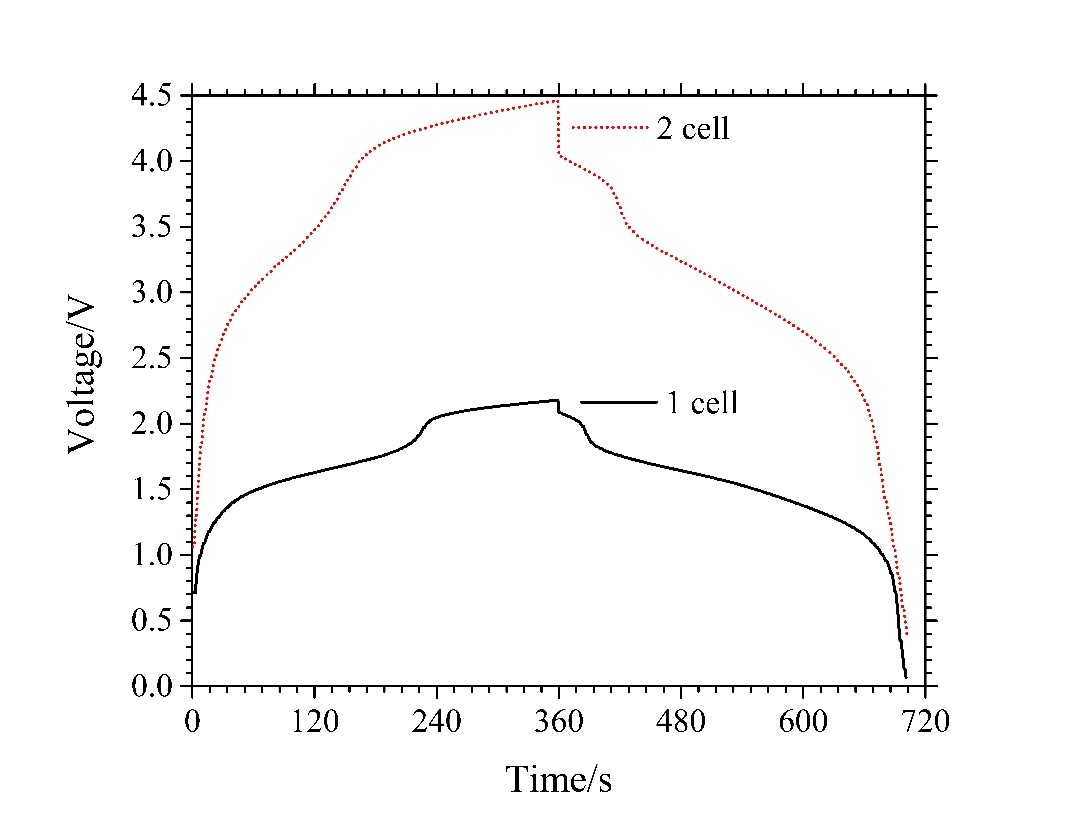


**Figure 7.** Performance of a balanced Al-ion cell consisting of TiO2 negative electrode, CuHCF positive electrode and 1 mol dm-3 AlCl3/mol dm-3 KCl electrolyte. A 20C charge/discharge rate was used.



**Figure 8.** Evolution of the charge/discharge profile of the aqueous Al-ion cell under extended cycling at 20C in 1 mol dm-3 AlCl3/1 mol dm-3 KCl.

A 2-cell aqueous Al-ion battery is also demonstrated using a bipolar electrode. The voltage vs. time profile is compared to a single cell in Figure 9. The charge and voltage efficiencies are comparable. Cycling at a 10C rate, the charge voltage increases steadily from circa 2.0 V to 3.5 V, at which point there is a more rapid increase in voltage to 4.1 V before a further steady increase to 4.5 V at the end of charge. During discharge, the voltage decreases steadily from 4.0 V to 3.7 V, at which point there is a rapid drop-off to 3.4 V followed by a more steady decline to 2.0 V at the end of discharge. From Figure 5, the two-voltage stages are associated with the CuHCF positive electrode. An average discharge voltage of 2.93 V was achieved, giving the battery an energy density of 14.8 mW h g-1 according to total mass of active material in both electrodes.



**Figure 9.** Typical profile of a 1-cell and 2-cell Al-ion battery cycled at a 10C charge/discharge rate in 1 mol dm-3 AlCl3/1 mol dm-3 KCl electrolyte.

# Conclusion

The first multi-cell battery based on aqueous aluminium ion chemistry is described. The battery is based on anatase (TiO2) nanopowder, CuHCF and aqueous Al3+/K+ electrolyte, which are all widely available, cheap and non-toxic materials, providing advantages over current Li-ion and Pb-acid systems. Although the specific energy is relatively low, ca. 15 mWh g-1 active material (combined positive and negative materials), a high charge and discharge rate of 20C is achievable. At the 20 C rate the energy efficiency of the cell remained above 70 % for over 1750 cycles, with only a 7 % capacity fade, demonstrating the longevity of the cell. The low specific energy is caused by the TiO2 anode; the capacity of CuHCF is c.a. 50 mAh g-1 at a current density of 333 mA g-1.

The charge storage capacity of TiO2 was shown to be due to the presence of Al3+ rather than the H+ present in the acidic electrolyte. However, the slight shift in neutron diffraction parameters is not sufficient to ascertain whether the main mechanism of charge storage is via Al3+ intercalation or a surface adsorption reaction. Further work on elucidating the mechanism could allow the cell capacity to be increased and the active materials to be tailored, for example towards high surface area materials for a surface process or doped materials for intercalation. Self-discharge exhibited by the TiO2 electrode, most likely due to the presence of dissolved oxygen, needs to be minimised and investigated further.

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1. Some coulombic efficiencies had to be estimated from charge/discharge cycles and assumed constant and accurate current densities as described. [↑](#footnote-ref-1)
2. From the charge-discharge cycle, of TiO2/Al cell, presented in the papers supplementary material. [↑](#footnote-ref-2)