**Aluminium-Poly(3,4-ethylenedioxythiophene) Rechargeable Battery with Ionic Liquid Electrolyte**

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# Abstract

Aluminium is one of the promising negative electrode materials for modern batteries. It is environmentally abundant, affordable and recyclable, and its three-electron redox reaction offers high theoretical specific energy and power. However, the development of a suitable positive electrode continues to limit the practical performance of aluminium batteries. In this study, the application of a 3D conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) as a potential positive electrode material is reported. The battery performance, C-rate versus capacity extraction and successive charge/discharge cycling of a full cell (aluminium (-); PEDOT (+); EMImCl-AlCl3 ionic liquid electrolyte) is investigated. The design of the PEDOT electrode (using 3D reticulated vitreous carbon as substrate) is studied, and is supported by microstructure characterisation. The aluminium-PEDOT battery provides 50-64 Wh kg-1 specific energy and 32-40 W kg-1 specific power. The battery has a coulombic efficiency >95 %, stable operation over 100 cycles and charge rates up to 80C. In summary, direct and meaningful progress has been made towards achieving useful capacity and cycling stability from aluminium batteries intended for future energy storage.



*Graphical abstract: Schematic illustration of the charging and discharging reaction of an aluminium-PEDOT battery with imidazolium-based chloroaluminate EMImCl-AlCl3 ionic liquid.*

# Keywords

3D electrode; aluminium battery; conductive polymer; ionic liquid electrolyte; poly(3,4-ethylenedioxythiophene) (PEDOT)

1. **Introduction and Broader Context**

Modern electronic technologies, such as electromobility, medical implants and robotics, are developing at an impressive pace, shaping modern societies by making our world more connected, safer and cleaner. However, reaching the full potential of such technologies heavily relies on the device that is powering them - the battery. Innovations in high-performance energy storage devices is somehow limited since the introduction of lithium batteries in the early 90s 1. This is mainly because of the trade-offs between performance, safety and sustainability. Never before has it been so important that energy storage devices employ sustainable, safe and low-cost materials. At the same time, such materials need to provide performance. Lithium-based batteries have a monopoly on specific energy and power performance (80-175 Wh kg-1 and 200-300 W kg-1) 2,3. Nevertheless, flammability, recycling difficulties and the limited availability of lithium and other constituents such as nickel and cobalt cause severe safety, cost effectiveness and future sustainability issues.

Aluminium-based batteries have the potential to minimise the trade-off between performance, safety and sustainability. Aluminium as a negative electrode material is lightweight, highly abundant and easy to recycle. It stands out for its safe cell reaction, non-flammability and non-toxicity, especially in combination with non-aqueous electrolytes such as ionic liquids. Due to the transfer of three electrons per charge/discharge cycle, the specific capacity of aluminium (3000 mAh g-1) is similar to lithium (3900 mAh g-1) 4.

The reversible deposition/dissolution of aluminium without the formation of a passivation layer is possible in non-aqueous electrolytes like chloroaluminate ionic liquids. They have the advantage of a wide potential stability window up to 4 V 5. Furthermore, the aluminium deposits are not prone to dendrite formation which might cause a short circuit of the battery 4,6. The state-of-the-art aluminium batteries with non-aqueous electrolytes such as 1-ethyl-3-methylimidazolium chloride (EMImCl-AlCl3) or 1,3-di-n-butylimidazolium bromide (BImBr-AlCl3) have positive electrodes made of graphite 6–9, oxides 10–15, sulphides 16,17, sulphur 18, zeolites 19 and conductive polymers 4,5,20,21. These charge storage materials host an ionic “guest species” from the electrolyte in their porous or layered structure. Graphite is the most popular material for positive electrodes in rechargeable aluminium batteries and was first demonstrated by Gifford et al. in the 80s 22. Aluminium-graphite batteries with Lewis acidic EMImCl-AlCl3 ionic liquid reach a high discharge potentials up to 2 V and a specific energy between 60 to 70 Wh kg-1 on average 6,7,23–25. However, the graphite electrode has to expand significantly to store the bulky guest ions between its layers, and cannot store anions in every layer, limiting its specific capacity. Meanwhile, sulphides, oxides and zeolite materials have low and rapidly decreasing discharge potentials 5.

A more advanced approach is to construct the positive electrode from a conductive polymer. This changes the charge storage mechanism from intercalation to insertion 26. Unlike graphite-based materials, conductive polymers combine faradaic and capacitive charge transfer by polymer oxidation/reduction and simultaneous insertion/removal of anions into the polymer structure. The insertion of anions during the charging (oxidation of the polymer) is accompanied by the expansion or swelling of the polymer film, offering more space to accommodate anions from the electrolyte 27. The amount of stored charges depends on the polymer film thickness, its accessible active area and synthesis method 28,29.

Previous studies demonstrate that PEDOT films electro-polymerised by cyclic voltammetry in Lewis neutral EMImCl-AlCl3 ionic liquid with EDOT monomer are stable at high potentials up to at least 2.5 V *vs.* Al|Al(III) and a minimum of 500 cycles, keeping a coulombic efficiency of 97 % without any morphological degradation in monomer-free Lewis neutral EMImCl-AlCl3 28,29. In contrast, PEDOT films cycled in a Lewis acidic composition show the formation of a viscous orange gel-like film after a few cycles, decreasing the capability of the anion insertion and removal process into the polymer 28. Therefore, PEDOT operates more efficiently in a Lewis neutral chloroaluminate ionic liquid composition.

The polymerisation potential window is crucial for the polymer performance. It has been shown that the anion insertion/removal at high potentials occurs only if the polymer was synthesised at the same high potentials (polymer “memory effect”) 28,29.

A previous proof-of-concept study of an aluminium-PEDOT battery in Lewis acidic chloroaluminate ionic liquid demonstrated feasibility but also serious limitations 21. The battery suffered from a very low cycle life as the PEDOT electrode degraded quickly. The reasons for this were the electro-polymerisation of PEDOT in aqueous solution with a narrow potential window and the overall Lewis acidic EMImCl-AlCl3 battery electrolyte which affects the polymer stability 21,28.

For the battery reported here, stable, high surface area PEDOT electrodes are used. PEDOT has been electro-polymerised in Lewis neutral EMImCl-AlCl3 on a three-dimensional reticulated vitreous carbon (RVC) network as studied in previous works 28,29. This approach prevents polymer degradation while maintaining the structural integrity of PEDOT. In addition, it has been demonstrated that PEDOT reaches higher charge/discharge potentials and is highly stable in Lewis neutral EMImCl-AlCl3 28, but the aluminium deposition at the negative electrode is only possible in a Lewis acidic ionic liquid composition. For this reason, a gradient in Lewis acidity of the electrolyte from negative to positive electrode has been introduced by soaking the porous PEDOT-RVC electrode in Lewis neutral ionic liquid and covering the aluminium surface with a Lewis acidic ionic liquid film.

This study offers a new approach for alternative battery systems exclusively designed with safe and sustainable materials. Thereby, the typical charge and discharge behaviour, stability and battery characteristic values are presented, showing the applicability of 3D PEDOT electrodes in aluminium batteries with performance characteristics useful for future energy storage.

* 1. **Aluminium-PEDOT Battery Concept**

The battery proposed in this work is composed of a metallic aluminium (negative electrode) and a conductive polymer (positive electrode) in an imidazolium-based chloroaluminate ionic liquid electrolyte 1-ethyl-3-methylimidazolium chloride-aluminium chloride (EMImCl-AlCl3). The battery operates by reversible deposition and dissolution of aluminium (Equation 1) at the negative electrode in a Lewis acidic chloroaluminate ionic liquid electrolyte, containing heptachlorodialuminate ions (Al2Cl7-) 5. Half-cell behaviour and electropolymerisation of PEDOT in chloroaluminate ionic liquid have been discussed in previous studies, forming the base for the here presented aluminium-PEDOT battery 27–29.

Negative electrode: Aluminium deposition and dissolution:

( 1 )

Early studies have demonstrated conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) as hybrid battery-(pseudo)-capacitor materials 26,30,31. They stand out for their low weight, low cost, high conductivity and capacity and straightforward electrochemical synthesis. Conductive polymers combine two kinds of energy storage mechanisms 27 (Figure 1). PEDOT chains, with an interchain distance *x1*, are in a neutral state of charge and non-conductive when uncharged (Figure 1 A). When PEDOT is charged/oxidised (Equation 2), positive charges are generated at specific monomer units (Figure 1 B). The generated positive charges are not located statically at a single atom of the polymer chain as PEDOT has a delocalised π-electron system. The oxidation of PEDOT is the faradaic (battery-like) reaction. If positive charges are generated in close vicinity to each other and at facing polymer chains, the chains are pushed away from each other because of repulsive forces between positively charged sites, increasing the inter-chain distance *x2*. Consequently, tunnels form between the polymer chains enabling the insertion of anions and formation of a double layer along the polymer chains. The anion insertion and compensation of positively charged sites are associated with the non-faradaic charges (capacitive charges). The inserted anions, especially tetrahedral AlCl4-, create transport paths and stretch the inter-chain distance *x3*based on their anion radius. PEDOT is fully charged when all positively charged sites are compensated by inserted anions (Figure 1 C). At this stage, the polymer should be stretched to its maximum, appearing as a swollen polymer morphology. At very high positive potentials an over-oxidation of the polymer can occur and lead to a degradation of the conductive polymer due to the nucleophilic attack of the electrolyte 5,32. When PEDOT is reduced/discharged, the charge transfer process is reversed. PEDOT loses its positive charged sites, inserted anions are removed subsequently as well as the double layer, and the polymer chain distances decrease again 27,33,34

The amount of inserted anions per monomer unit is determined by the generated and accessible charged sites in the polymer, increasing with the charging potential. The number of inserted anions per monomer unit is described as degree of insertion α (α = 0 to 1) 28,35,36.

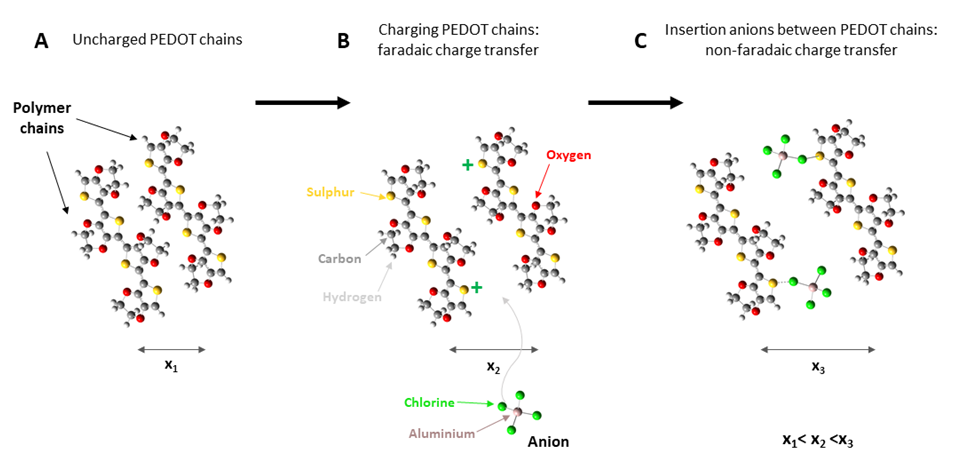


Figure 1: Illustration of two PEDOT chains (A) in the uncharged state, (B) during charging/oxidation and (C) in a fully charged state. The inter-chain distance x increases during charging of PEDOT (faradaic charge transfer) and insertion of anions (non-faradaic charge transfer).

Furthermore, the formation of charged sites depends also on the polymer morphology, which is pre-determined and controlled by the method of electro-polymerisation, applied potential and inserting anions 27,28. In contrast to conductive polymers synthesised in aqueous solution or in organic solvents such as acetonitrile, polymer films produced in ionic liquids show higher cycle stability with a highly reversible anion insertion/removal reaction and formation of charged sites at high electrode potentials leading to better battery performance 4,5,28,37–40.

Positive electrode: Conductive polymer oxidation/anion insertion and reduction/anion removal):

( 2 )

The overall reaction of an aluminium-PEDOT battery (Equation 3):

( 3 )

1. Experimental Methods
   1. **Electro-Polymerisation of PEDOT Electrodes**

The electro-polymerisation of EDOT was performed by cyclic voltammetry from 0 V to 2.4 V *vs.* Al|Al(III) in Lewis neutral 1-ethyl-3-methylimidazolium chloride-aluminium chloride (EMImCl-AlCl3) (*χ*(EMImCl):*χ*(AlCl3) = 50 mol-%:50 mol-%) with 0.1 mol dm-3 3,4-ethylenedioxythiophene (EDOT) (Alfa Aesar; 97 %) at 100 mV s-1, over 10 cycles at 25°C according to Schoetz et al. 28. The polymer was rinsed with monomer-free Lewis neutral EMImCl-AlCl3 after polymerisation to remove residual monomer on the electrode surface. Polymerisation was carried out in a three-electrode-cell (EL-CELL; PAT-Core cell with single PAT-Cell) (Figure 1) fitted with a planar vitreous carbon disc (counter electrode; Micro to Nano; surface area 1.2 cm2, 2 mm thickness), a reticulated vitreous carbon (RVC) disc (working electrode and PEDOT substrate; Duocel, ERG Aerospace; three-dimensional area 2.1 cm2 41,42, 2 mm thickness) and an aluminium ring (EL-CELL; 99.99 %) as reference electrode. Counter and working electrode were separated by a glass fibre disc (Whatman; surface area 1.2 cm2, 0.1 mm thickness) soaked with the polymerisation electrolyte. The RVC substrate was previously soaked in the polymerisation electrolyte to ensure a homogeneous polymerisation in the pores of the material29. After the cyclic voltammetry, a 3 µm thick PEDOT film on the struts of the RVC with an overall polymer surface of 2.1 cm2 was obtained. Assuming that the density ρ(PEDOT)≈(EDOT), the film has a volume of 6.3 ×10-4 cm3 and mass of 0.84 mg (≡ 0.4 mg cm-2 PEDOT loading per area of RVC) in the uncharged state. The RVC acts as a chemically and electrochemically inert substrate for the polymer and does not intercalate or insert any electrolyte ions 28. The aluminium current collector at the positive electrode is covered with a protective conductive carbon-coated aluminium foil to avoid contact between ionic liquid electrolyte through the pores of the RVC-PEDOT electrode and the aluminium surface. The foil does not intercalate ionic species of the ionic liquid and is chemically inert.



*Figure 2: Schematic illustration of the electrochemical test cell and assembly.*

* 1. **Battery Cycling**

The same cell, but without the reference electrode, was used for the full cell battery cycling experiments. The positive electrode was the previously prepared PEDOT on RVC (section 2.1) soaked in monomer-free Lewis neutral EMImCl-AlCl3 (*χ*(EMImCl):*χ*(AlCl3) = 50 mol-%:50 mol-%) and the negative electrode was an aluminium disc (Alfa Aesar; 99.997 %, 1.2 cm2, 0.1 mm thickness). The Lewis neutral ionic liquid remains in the pores of the PEDOT-RVC electrode due to its viscosity. The aluminium electrodes were polished with fine abrasive paper and rinsed with Lewis acidic EMImCl-AlCl3 before battery cycling. A glass fibre separator (Whatman; 1.2 cm2, 0.1 mm thickness) was soaked in Lewis acidic EMImCl-AlCl3 (Sigma-Aldrich) (*χ*(EMImCl):*χ*(AlCl3) = 33 mol-%:67 mol-%) and placed between the positive and negative electrode.

The battery was charged at constant current until a cut-off potential of 2.2 V. The potential was subsequently held until the current reached 0.15 mA (constant current constant voltage (CCCV) charging procedure). The cut-off potential for the constant current discharging was 0.5 V. The batteries were charged and discharged at different current rates from 0.1 mA to 10 mA (from 0.8C to 80C) and -0.1 mA to -1 mA (0.8C, 4C to 8C), respectively. High C-rates were chosen to demonstrate the remarkable power capability of the battery.

The used ionic liquids are hygroscopic and need to be handled in an inert atmosphere with ≤500 ppm water content in solution in order to maintain their electrochemical and chemical stability 6. Therefore, a glove box with a nitrogen atmosphere (MBraun, UNIlab Pro Eco, <0.5 ppm water and <0.5 ppm oxygen) at 25°C was used for the electro-polymerisation and battery cycling experiments. All electrolytes were dried under vacuum at 60 °C for at least 24 h.

* 1. **Scanning Electron Microscopy**

The morphology of PEDOT and aluminium electrodes before and after battery cycling (after 100 cycles) were investigated by scanning electron microscopy (SEM; LEO 1450VP and JEOL JSM 6500F). The samples were rinsed beforehand with dimethyl carbonate and dried in vacuum for at least 1 h.

1. Results and Discussion
   1. Characteristic Charge and Discharge Behaviour

The charge and discharge curve for an aluminium-PEDOT battery (Figure 2) shows several plateaus between 0.5 V and 2.2 V 27. The open-circuit potential in the fully charged state is 2.1 V. The low potential drop of 100 mV between the charging and starting discharge potential shows the good conductivity of the combination of Lewis neutral EMImCl-AlCl3 in the PEDOT electrode and Lewis acidic EMImCl-AlCl3 at the aluminium electrode, forming a gradient in electrolyte acidity between the electrodes.



*Figure 3: Characteristic charge and discharge cycle of an aluminium-PEDOT battery charged with 0.1 mA (0.8C) until 2.2 V and discharged with -0.1 mA (0.8C) until 0.5 V at 25°C.*

*Battery Charging:*

The aluminium-PEDOT battery shows a steady increase in potential until 1.5 V when charged at 0.1 mA (0.8C) (Figure 2, area I). A charging plateau cannot be observed in this potential window because the insertion of anions only occurs at potentials above 1.5 V as shown in a previous study with electrochemical quartz crystal microbalance measurements 27. In the potential range from 0.5 V to 1.5 V the anion insertion paths within the polymer widen 27. Previous research evidence suggests this is probably due to the formation of repulsive positive charges in the polymer backbone by oxidation. The starting anion insertion is shown by two potential dips in the charging curve between 1.5 V and 1.7 V (Figure 2, area II). There is a slightly increasing plateau until the cut-off potential of 2.2 V, showing the enhanced insertion of anions (Figure 2, area III). At this stage, the PEDOT is oxidised and swollen, enabling the accommodation of high concentrations of AlCl4- anions from the Lewis neutral ionic liquid.

*Battery Discharging:*

The discharge curve starting at 2.1 V is slightly sloping in the potential window from 2.1 V to 1.4 V (Figure 2, area I) when discharged at -0.1 mA (0.8C). In this potential window, the anion removal from the polymer backbone is fast, as the paths between polymer chains are still swollen and open 27. The formation of the sloping plateau with an average discharge potential of 1.75 V correlates with capacitive-like behaviour of PEDOT observed at this state of charge/discharge 27. It follows a smaller discharge plateau around 1.4 V (Figure 2, area II) and a strong drop of the discharge potential from 1.3 V to 0.7 V (Figure 2, area III). This is related to the contraction of the paths between the polymer chains 27. A constant discharge plateau at 0.6 V (Figure 2, area IV) indicates the battery-like behaviour of PEDOT at a lower state of charge/discharge.

* + 1. Battery Characteristics

Batteries are characterised by their specific values such as capacity *Qspec*[Ah kg-1], energy *Espec* [Wh kg-1] and power *Pspec* [W kg-1] per unit active mass *ma* (Equation 4-6). The average discharge potential *E*, applied discharge current *I* and discharge time *t* have been used to calculate the following specific values.

( 4 )

( 5 )

( 6 )

PEDOT and aluminium are both low-weight materials, not least because of the three-dimensional structure of PEDOT and its high active surface area per unit volume and mass. The battery characteristic values have been determined for three different cases (Table 1) in terms of considered active mass *ma* in order to enable a fair comparison between the reported specific energy and power of state-of-the-art and other aluminium-based batteries 6,7,23,43.

The specific capacity of the used PEDOT electrode is 191 mAh g-1 if the whole mass of polymerised PEDOT on RVC and a battery discharge capacity of 0.16 mAh is considered (Figure 2). This demonstrates a capacity that indicates that every monomer unit present carries a single positive charge. However, it is not suggested that all of these charges are balanced by an inserted anion. From previous research, the maximum degree of anion insertion *α* is 0.33 28,35,36. Therefore, PEDOT clearly indicates a combination of faradaic and capacitive charge storage in the proportion of 2:1 capacitive to faradaic charge storage, achieving 63.6 mAh g-1 through faradaic storage and 127.2 mAh g-1 capacitive storage. The specific capacity of PEDOT (191 mAh g-1) used in this work is about 50 mAh g-1 higher than the highest achieved for graphite (142 mAh g-1) in aluminium batteries with chloroaluminate ionic liquid 23.

PEDOT can be designed to accommodate a variable amount of anions by adapting film thickness, substrate dimensions and shape. PEDOT also expands during charging 27, providing a higher capacity as more monomer units become accessible for inserting anions. However, the positive electrode is designed so that there is no overall volumetric change. PEDOT expands and contracts around the struts of the RVC, which acts as a rigid substrate. The mesoporous structure of the RVC provides space for PEDOT to change its volume internally in the positive electrode while maintaining the electrode’s overall dimensions. This is a more practical method of accommodating expansion than graphite, where the full volume of the electrode expands and contracts.

*Case 1) Active species:* This case considers only the mass *ma* (Equation 7) of active species that actively take part in the battery reaction (Equation 3):

( 7 )

Total mass of PEDOT (Equation 8) is considered to be the mass polymerised around the struts of the RVC with an overall polymer film area 42 *Af* of 2.1 cm2 and film thickness 29 *hf* of 3 µm. It is assumed that the density of PEDOT is similar to the density of one EDOT monomer unit (ρ(EDOT)≈ρ(PEDOT) with molar mass EDOT M(EDOT)=142 g mol-1) 27.

( 8 )

The mass of Al2Cl7- anions (Equation 9) is determined by the deposited mass of aluminium during constant current charging Qcharge=0.16 mAh (Figure 2). The deposited mass of aluminium in the fully charged state was calculated via the Faraday equation (with number of transferred electrons z=3 and Faraday constant F=96485 As mol-1).

( 9 )

*Case 2) Active species with insertion anions:* Here the mass *ma of* active species like in case 1 with inserting AlCl4- anions from Lewis neutral EMImCl-AlCl3 in the PEDOT electrode (Equation 10) is considered. This is similar to the approach taken by Wang et al. 43.

( 10 )

As the unique feature of the presented aluminium-PEDOT battery is the simultaneous oxidation/reduction of PEDOT and the insertion/removal of AlCl4- anions into the polymer structure, the mass of inserting anions *ma(AlCl4-)* (Equation 11) should be also considered, based on a degree of anion insertion of 0.33. AlCl4- is the only inserting anion as at the positive electrode a Lewis neutral EMImCl-AlCl3 is present, which is soaked into the conductive polymer.

( 11 )

*Case 3) All species:* Finally, the mass *ma* of all species in the battery is considered. This includes also “dead mass” such as EMIm+ cations, according to the method of Kravchyk et al. 23. This method is designed to account for the depletion of electrolyte species during charging, where Al2Cl7- reacts to aluminium and AlCl4-. The latter is then extracted from the electrolyte and stored in the positive electrode. The following equation (Equation 12) for specific capacity of the whole electrolyte and PEDOT electrode is taken from Kravchyk et al. 23. In this equation, F is Faraday constant, is the number of electrons involved in reducing 1 mol of AlCl3, *r* is the maximum molar ratio of the electrolyte, *QC* is the specific capacity of the positive electrode (in mAh g-1), and *M(AlCl3)* and *M(EMImCl)* are the molar masses of AlCl3 and EMImCl.

38.76 mAh g-1 ( 12 )

This specific capacity (39 mAh g-1) and the overall charge capacity of the battery (0.16 mAh) are then used to calculate the active mass *ma* to be considered for the specific energy and power for case (3).

*Table 1: Calculated active mass, specific capacity, energy and power for an aluminium-PEDOT battery at a charge and discharge rate of ± 0.1 mA (0.8C) (Figure 2).*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Case | Active mass  *ma*/ kg | Specific capacity,  *Qspec*/ Ah kg-1 | Specific energy,  *Espec*/ Wh kg-1 | Specific power,  *Pspec*/ W kg-1 |
| 1) Active species | 3.24×10-6 | 49 | 64 | 40 |
| 2) Active species with insertion anion | 3.57×10-6 | 41 | 58 | 36 |
| 3) All species | 4.13×10-6 | 39 | 50 | 32 |

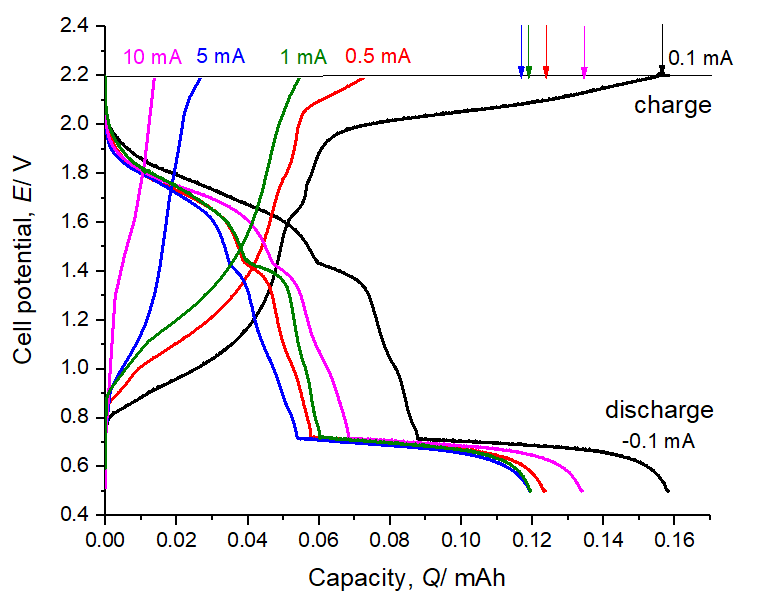
The calculated performance of the aluminium-PEDOT battery is similar to other reported aluminium-based batteries with chloroaluminate ionic liquid electrolyte. Using a method comparable to case (2), aluminium-graphite batteries have achieved 69 Wh kg-1 43, whereas using a method comparable to case (3), a specific energy of 65 Wh kg-1 23 has been reported for the half-cell. The increase in specific energy compared to aluminium-PEDOT is due to the higher average discharge potential of aluminium-graphite (~1.77 V *vs.* 1.3 V).

For the purpose of comparison, the specific capacity, energy and power for an active mass only of the deposited mass of aluminium and PEDOT are 179 Ah kg-1, 233 Wh kg-1, and 146 W kg-1. Taking into account also the inserting anions AlCl4- at the positive electrode for a degree of insertion of 0.33, the values reduce to 56 Ah kg-1, 73 Wh kg-1 and 46 W kg-1.

Considering only the positive electrode, PEDOT shows theoretically better performance than graphite with a higher specific capacity and better volume change characteristics. Nevertheless, the limiting factor is not the material of the positive electrode. The specific capacity, energy and power are determined by the amount of chloroaluminate ionic liquid required to provide the charged species for battery operation. In order to improve the battery performance with a chloroaluminate ionic liquid, the cell potential needs to be increased instead. The cell potential can be improved by modifying the electrolyte, e.g. via gelification of the ionic liquid, increasing the potential stability window. Currently, the ionic liquid starts to decompose when charged frequently over 2.3 V. Therefore, the limiting charging potential is 2.2 V. If the potential window of a Lewis neutral chloroaluminate ionic liquid with solely AlCl~~4~~- anions can be increased by 1 V, the deposition of aluminium from AlCl4- would be possible, reducing the required mass of electrolyte significantly.

* + 1. Charge Rates

The aluminium-PEDOT battery has been charged and discharged with an increased charge rate from 0.1 mA to 10 mA (0.8C to 80C) until 2.2 V and subsequently held at 2.2 V until the cell current reached 0.15 mA. The corresponding discharge curves (-0.1 mA, 0.8C) were compared (Figure 3).

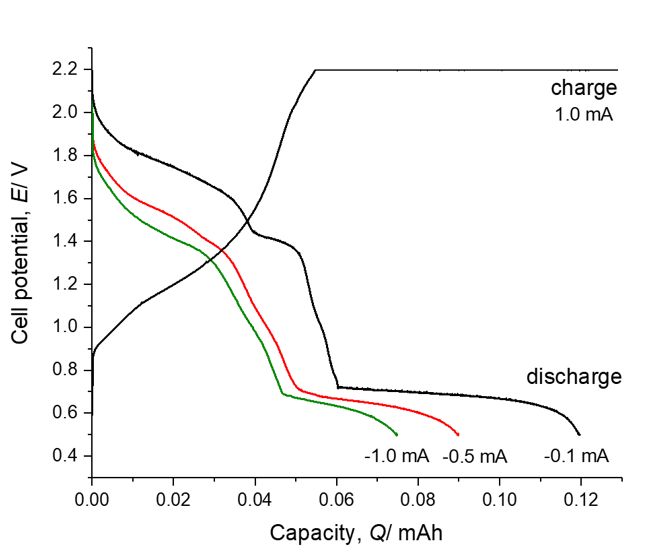


*Figure 4: Charge and discharge curves of an aluminium-PEDOT battery charged with 0.1 mA (0.8C, black line), 0.5 mA (4C, red line), 1.0 mA (8C, green line), 5.0 mA (40C, blue line) and 10 mA (80C, pink line) until 2.2 V, held at constant potential of 2.2 V until 0.15 mA (end of charge marked by arrows) and discharged with -0.1 mA (0.8C) until 0.5 V at 25 °C.*

For all charge rates, the charge capacity is equal to the corresponding discharge capacity. The capacity is highest when the cell is charged slowly at 0.1 mA (0.8C), which is the expected behaviour. However, a linear decrease of the capacity with increasing charge rate is not observed. When the cell is charged at 10 mA (80C) it delivers a still higher capacity when charged with 5 mA (40C), 1 mA (8C) or 0.5 mA (4C). This might be related to morphological changes of the polymer such as polymer swelling and contraction during charging/discharging and accompanied anion insertion/removal 27. With increasing charging rate, the cut off potential of 2.2 V is reached faster but the constant potential phase until the battery is fully charged (at 0.15 mA) is longer. The battery seems more efficient when charged primarily at constant current, enabling a better anion insertion and higher capacity 27.

* + 1. Discharge Rates

The battery was charged at 1 mA (8C) to 2.2 V, held at constant potential of 2.2 V until current decreased to 0.15 mA and discharged at -0.1 mA (0.8C), -0.5 mA (4C) and -1 mA (8C) (Figure 4). The battery shows the same characteristic discharge behaviour for all discharge rates. The extracted capacity decreases about 37 % when discharged at -1 mA (8C) in comparison to -0.1 mA (0.8C).



*Figure 5: Charge and discharge curves of an aluminium-PEDOT battery charged with 1.0 mA (8C) until 2.2 V, held at constant potential of 2.2 V until 0.15 mA and discharged with -0.1 mA (0.8C), -0.5 mA (4C) and -1.0 mA (8C) until 0.5 V at 25 °C.*

* 1. Cycle Stability

The aluminium-PEDOT battery was charged with 1 mA (8C) until 2.2 V, held at this potential until the cell delivered 0.2 mA, and discharged at -0.1 mA (0.8C) until 0.5 V for 100 cycles. The coulombic efficiency of one charge and discharge cycle (*Q*charge/*Q*discharge) ranges between 94 % and 99 % (Figure 5). This demonstrates the reversibility of the electrode reactions (Equation 1), electrode stability and maintenance of the electrolyte acidity gradient.



*Figure 6: Coulombic efficiency of the charge and discharge reaction of an aluminium-PEDOT battery depending on the cycle number. The battery was charged with 1.0 mA (8C) until 2.2 V and discharged with -0.1 mA (0.8C) until 0.5 V at 25°C.*

The coulombic efficiency of the first cycle (≥93 %) is lower than the average value as the efficiency increases to >95 % over the following cycles. It seems that the coulombic efficiency fluctuates periodically every 20 cycles by 6 %. This is related to the morphological and viscoelastic changes which the polymer electrode undergoes when charged and discharged 27,33,34. The change of the polymer characteristics is caused by polymer swelling and contraction phenomena, which has been explained by the generation and removal of repulsive forces between the monomer units, accompanied by anion insertion and removal in the polymer backbone. The charging reaction causes a swelling and merging of the polymer grains as well as a softening of the film 27. This enables a fast charge transfer of anions at a high state of charge, which produces non-faradaic behaviour like a capacitor.

Furthermore, the swelling of the polymer has the effect of widening the transport paths for anions, storing more charges in the polymer and delivering a higher capacity. The discharge reaction is characterised by contraction and separation of the previously merged polymer grains, whereas the grains relocate from their initial position with decreasing state of charge. At the same time, the polymer regains its stiffness and pronounced faradaic behaviour like a battery. The shear modulus (softness/stiffness) of the polymer film does not return to its initial value after every cycle 27. PEDOT remains swollen to a certain extent 27. It seems that it takes about 20 cycles for the polymer to return to its initial shear modulus.

The morphology of the PEDOT (Figure 6) and aluminium (Figure 7) electrodes were investigated by SEM; both before battery cycling and after 100 cycles. The struts of the RVC are coated with an up to 3 µm thick layer of PEDOT 29 consisting of grains with an average diameter of ≤1 µm. The SEM images before (Figure 6 B) and after (Figure 6 C) battery cycling show no significant change in morphology, no detachment of the polymer film or degradation. This observation is consistent with previous studies when PEDOT has been cycled over 500 times in Lewis neutral EMImCl-AlCl3, maintaining a coulombic efficiency of the anion insertion/removal of 97 %29.



*Figure 7: PEDOT: SEM images of (A) bare RVC. (B) PEDOT on RVC, before battery cycling. (C) PEDOT on RVC, after battery cycling (charge CCCV: 1 mA (8C) until 2.2 V, 2.2 V until 0.15 mA; discharge CC -0.1 mA (0.8C) until 0.5 V) for 100 cycles.*

The aluminium deposition on the negative electrode was carried out on polished high purity aluminium substrates (Figure 7 A). After 100 charge and discharge cycles, a clear aluminium deposit is visible (Figure 7 B-D). The aluminium deposits appear as spherical grains with an average size of ≤5 µm which is typical for aluminium deposits in ionic liquids and the low current densities at the negative electrode ≤10 mA cm-2 7,8,21,44–46. The grains agglomerate over the electrode surface, forming flower-like structures with an average diameter of ≤50 µm. Dendrite growth, which could lead to a short circuit of the battery, has not been observed.



*Figure 8: SEM images of (A) pure aluminium surface before and (B-D) after battery cycling (charge CCCV: 1 mA (8C) until 2.2 V, 2.2 V until 0.15 mA; discharge CC -0.1 mA (0.8C) until 0.5 V; 100 cycles) with aluminium deposit.*

1. Conclusions

This research studied the cycling characteristics and behaviour of a rechargeable aluminium-PEDOT battery in chloroaluminate ionic liquid electrolyte:

1. The aluminium-PEDOT battery can be charged and discharged reversibly in the potential window of 0.5 V to 2.2 V.
2. The calculated battery characteristic values such as specific energy and power are in the range of 50-64 Wh kg-1 and 32-40 W kg-1.
3. The cell reaches a high cycle stability over 100 cycles with a coulombic efficiency ≥95 % and shows no morphological degradation of the PEDOT or aluminium electrode surface.
4. The battery can be charged and again discharged over a wide range of charge rates; also at high rates up to 80C.

In general, the limiting factor in terms of specific capacity, energy and power of aluminium-based batteries is the Lewis acidic chloroaluminate ionic liquid with bulky Al2Cl7- anions and the narrow potential stability window. Therefore, modifications and improvements of the electrolyte would be the next reasonable step for aluminium batteries.

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