



Investigation of different anode materials for aluminium rechargeable batteries



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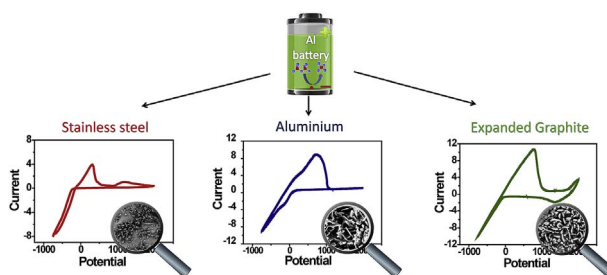
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HIGHLIGHTS

- Reversibility of Al reduction-oxidation reaction is evaluated in Al, SS and carbon.
- Expanded graphite is very promising due to its dual role as anode and cathode.
- 3D substrates have higher efficiencies and smaller overpotentials for Al reaction.
- 3D substrates are more suitable for rechargeable Al-batteries with higher power.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to shed some light into the importance of the anodic reaction in reversible aluminium batteries, we investigate here the electrodeposition of aluminium in an ionic liquid electrolyte (BMImCl-AlCl₃) using different substrates. We explore the influence of the type of anodic material (aluminium, stainless steel and carbon) and its 3D geometry on the reversibility of the anodic reaction by cyclic voltammetry (CV) and galvanostatic charge-discharge. The shape of the CVs confirms that electrodeposition of aluminium was feasible in the three materials but the highest peak currents and smallest peak separation in the CV of the aluminium anode suggested that this material was the most promising. Interestingly, carbon-based substrates appeared as an interesting alternative due to the high peak currents in CV, moderate overpotentials and dual role as anode and cathode. 3D substrates such as fiber-based carbon paper and aluminium mesh showed significantly smaller overpotentials and higher efficiencies for Al reaction suggesting that the use of 3D substrates in full batteries might result in enhanced power. This is corroborated by polarization testing of full Al-batteries.

1. Introduction

In the last few years, the development of aluminium batteries has been attracting the attention of scientists worldwide. This growing interest is triggered by the high theoretical gravimetric capacity of aluminium (2.98 Ah g⁻¹), comparable with lithium (3.86 Ah g⁻¹), its

volumetric capacity (8.04 Ah cm⁻³) being four times higher than that of lithium (2.05 Ah cm⁻³), its low cost, high abundance and safety [1,2]. Primary Al-air batteries based on aqueous electrolytes have been investigated since the 1960s [3]. However, it is likely that alternative electrolytes should be considered with respect to developing *rechargeable* Al-batteries. This is due to the hydrogen evolution in aqueous

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electrolytes that hinders any possible Al electrodeposition of metallic Al (-1.68 V vs SHE) during the recharging of the battery. Therefore, one of the most important challenges of Al-battery technology is the development of electrolytes with high electrochemical stability that can allow the reversible electrodeposition of aluminium.

Since the 1990s, a large number of investigations have reported on the lab-scale electrodeposition of aluminium using nonaqueous electrolytic systems [4–6]. Chloroaluminate-based ionic liquids (ILs), formed by adding AlCl_3 to organic halides such 3-dialkylimidazolium chloride, alkylpyridinium chloride or quaternary ammonium chloride, are recognized electrolytes for aluminium electrodeposition at room or nearly room temperature [7–11]. These ILs show adjustable Lewis acidity over a wide range of molar ratios of AlCl_3 to organic chloride (MCl). When the molar ratio of AlCl_3/MCl is more than 1 (Lewis acid), the dominant species in the electrolyte is the Al_2Cl_7^- ion which is electrochemically active and can be reduced to metallic Al. However, the drawback of these electrolytes are due to their hygroscopic character and their high reactivity with ambient humidity that provokes the violent evolution of acidic and corrosive vapours. Although many other electrolytes have been explored as more stable alternatives; namely, amides (such as urea or acetamide) [12], glymes [13,14], bistrifluorosulfonyl-based ILs [15] among others [16,17]; none of these surpass the performance of chloroaluminate-based ILs for aluminium electrodeposition.

It should be note that most studies on Al electrodeposition have been focused on the metallurgical aspects of the deposition such as the quality of the deposits in terms of purity, roughness, crystal size, aspect and morphology [18–20]. However, the reversibility of the reaction and the efficiency of the electrochemical process, which are of paramount importance for batteries, have not been investigated in detail. Probably due to the better electrochemical behaviour of chloroaluminate-based ILs, the vast majority of these Al rechargeable batteries utilize the so-called “first” generation of ILs. In those examples that include both Al-ion [21,22] and Al-air batteries [23], the reversibility of the battery for a limited number of cycles and at moderate operating currents has been demonstrated. Although the scientific community has been quite interested in the cathodic reactions [24–28] of these reversible Al batteries, to the best of our knowledge, there is no significant research dealing with the influence of the anodic reaction in battery performance.

In this work, we investigate the electrochemical reaction of aluminium in chloroaluminate-based ILs to obtain a better understanding of the anodic reaction of a reversible Al-battery. Not only the electrodeposition of aluminium but also the reversibility of the reaction in $\text{BMImCl}:\text{AlCl}_3$ (1:2 M ratio) were systematically investigated by using cyclic voltammetry and galvanostatic charge-discharge techniques. The impact of both the chemical nature and geometry of the anode on the reversibility of the reaction and consequently on the battery performance were investigated using different materials (aluminium, stainless steel and carbon) and different geometries. To our knowledge, this is the first time that materials different from aluminium are proposed as anode for reversible Al-batteries.

2. Experimental

2.1. Materials

Granular Aluminium trichloride (AlCl_3) was purchased from Fluka (> 99%) and 1-butyl-3-ethylimidazolium chloride (BMImCl) (98%) was purchased from Solvionic. Aluminium foil (99.999%) was obtained from Sigma Aldrich. The aluminium mesh alloy 5052 (96.2%), stainless steel foil (AISI 302), stainless steel mesh (AISI 316), aluminium wire (99.999%) and aluminium foam (98.5%) were purchased from Goodfellow. Expanded Graphite was obtained from SGL carbon. Toray carbon paper TGP-H-60 was purchased from Alfa Aesar, Vulcan XC7212 carbon was obtained from Cabot Corporation whereas MnO_2 (~85%)

and Polytetrafluoroethylene (PTFE) (60 wt % dispersion in H_2O) were purchased from Sigma Aldrich.

2.2. Electrolyte preparation

The electrolyte was prepared in a glove box by slowly adding AlCl_3 to BMImCl at a molar ratio of 2:1 ($\text{AlCl}_3:\text{BMImCl}$) while stirring using a magnetic bar at room temperature, according to the procedure explained elsewhere [8]. While that process is taking place, the two solids turn into a yellowish transparent liquid.

2.3. Electrochemical tests

Electrochemical tests were performed at room temperature in an Ar-filled glove box ($\text{H}_2\text{O} < 0.5$ ppm and $\text{O}_2 < 1.5$ ppm) and using a Biologic Potentiostat/Galvanostat (Biologic SP-150). Aluminium foil, aluminium mesh, stainless steel and expanded graphite with a geometrical area of 1 cm^2 were used as working electrode in an in-house designed 3-electrode cell with fixed distance between the three electrodes and a 2 mL volume for the electrolyte. Aluminium foam and aluminium wire were employed as counter and reference electrodes, respectively. Prior to use, aluminium materials and stainless steel foil were cleaned for 15 min in an acidic mixture whose composition was a 70% H_3PO_4 (85% in water), 25% of H_2SO_4 (98% in water) and 5% of HNO_3 (52.5% in water). Subsequently, the samples were cleaned with distilled water and dried in a vacuum oven for 4 h. In order to eliminate any remaining impurities, the working electrodes were pre-treated electrochemically by cyclic voltammetry from 1 to 3 V at high scan rate (100 mV s^{-1}) as reported elsewhere [8].

Electrodeposition of aluminium onto the different substrates was firstly investigated by cyclic voltammetry (CV) measurements performed in $\text{AlCl}_3\text{-BMImCl}$ (2:1) electrolyte from -0.75 V to 2 V at different scan rates (at 50, 20, 10 and 5 mV s^{-1}) in 3-electrode electrochemical cells. Polarization tests consisted of consecutive galvanostatic reduction-oxidation cycles of 30 min at increasing currents (from $\pm 0.2\text{ mA cm}^{-2}$ to $\pm 7.5\text{ mA cm}^{-2}$) and were also performed in 3-electrode cells. Constant current electrodeposition of aluminium was performed applying a current density of -0.5 mA cm^{-2} for 180 min onto the three different substrates.

2.4. Characterization of aluminium electrodeposits

SEM and EDX analysis were performed using a Table Top Microscope (Hitachi TM-1000) whereas XRD was obtained with a Philips PW 3040/00 X'Pert MPD/MRD diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$).

2.5. Assembly and electrochemical performance of the aluminium battery

Aluminium batteries were assembled using MnO_2 as a cathode, $\text{AlCl}_3:\text{BMImCl}$ (2:1) as the electrolyte and two different types of aluminium geometries (foil and mesh) as anode. The cathodic paste was composed of vulcan carbon, PTFE and MnO_2 (2:1:3 in weight) and was deposited onto stainless steel mesh. The geometrical area of cathode was twice that of the anode to ensure that battery performance would be limited by the aluminium anode. Galvanostatic polarization tests were performed during battery discharge applying increasing current densities from 0 to -4 mA cm^{-2} with an increment of 0.25 mA cm^{-2} in steps of 30 s.

3. Results and discussion

3.1. Effect of substrate materials on Al electrodeposition

In all publications to date, only aluminium foil has been used as the anode in Al-batteries. In order to investigate alternatives that might

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