Al-ion Battery Based on Semi-Solid Electrodes for Higher Specific Energy and Lower Cost

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Section 1. Areal capacity in Al-ion batteries: state of the art.

The areal capacities demonstrated in literature are summarized in **Figure S1**. One can see that there is room for lowering battery cost by achieving areal capacities higher than those values.



Figure S1. Energy cost vs Areal capacity using W as current collector. Energy cost for areal capacities reported in literature^{1–8}.

Section 2. Experimental section

<u>2.1 Materials</u>

A commercial mixture of AICl₃ : EMImCl (\leq 100 iron ppm) with a molar ratio of 1.5 (*r* =1.5), synthetic graphite powder (SGP) and the binder (PTFE - 60 wt% dispersion in water)were purchased from Sigma-Aldrich. Synthetic graphite flakes (SGF) powder was obtained from IMERYS. And finally, Aluminiumn (AI) foil (99.9995%) and Tungsten (W) foil (99.95%) were purchased from Alfa Aesar.

2.2 Preparation of semi-solid cathode

Semi-solid cathodes were prepared in an Ar-filled glovebox (Braun) with controlled water and oxygen content ($O_2 < 1.2$ ppm and $H_2O < 0.6$ ppm). 3 ml of electrolyte was added to a syringe and immediately 1 g of graphite powder was incorporated. This mixture was stirred for a minute using a Pro Scientific Ultra-turrax Model PRO20. After that, 1 g of graphite (or the remaining amount) was again added to the mixture and then it was stirred again during a minute. This step will be repeated several times until the desired content of active material was reached. Table S1 shows the composition of the studied slurries. The electrode porosity was calculated as volume electrolyte / volume electrolyte + volume

graphite, taking 2.2 g cm⁻² as bulk density of graphite.

Slurry	SPG content	SPF content	Electrolyte Volume	Electrode
Mixture	(g)	(g)	(ml)	Porosity (%)
100SGP	2.5	0	3	72
95SGF:5SGP	0.25	4.5	3	58
100SGF	0	5	3	57
M23	1.75	0	3	79
M20	2	0	3	77
M26	2.25	0	3	75

 Table S1. Composition and porosity of the slurries used in this work.

2.3 Electrochemical characterization of semi-solid cathode

In order to study the electrical conductivity of semi-solid cathodes, electrochemical impedance spectroscopy (EIS) was used in two-electrode configuration (separator-free symmetrical cell) for each mixture. A schematic drawing of the set up can be found bellow, **Figure S2.** The symmetrical cell consists of two Teflon plates that serve as package; two

W foils, as blocking current collector, and one Viton joint with a rectangular cavity of 8

cm² and a thickness of 1 mm. This space (0.8 mL) is filled with the semi-solid cathode.

And finally, the cell is closed with the help of a screws system.



Figure S2. Symmetrical electrochemical cell designed for impedance of Semi-solid cathode.

2.4 Electrochemical characterization of Semi-solid Al-ion batteries.

The semi-solid Al-ion batteries is constituted by two Teflon plates as package, the negative current collector was a mesh of Al onto an Al foil to ensure that the electrodeposition of Al occurs in a high surface area and, thus, the limited part of the battery is the positive side. A Whatman glassfiber soaked in electrolyte was used as separator. The semi-solid cathode was pasted onto the W positive current collector

covering an area of 8 cm⁻² and the volume was controlled by a gasket of Viton® of 1 mm of thickness. In order to study the influence of electrode thickness, cell assembled with 2 and 4 mm were assembled. To compare the performance of semi-solid batteries and conventional batteries, three cells were assembled using a solid cathode composed by graphite and PTFE in a proportion of 9:1 and with 1, 2 and 4 mm thickness, respectively. Then the cells were closed using two Teflon plates fixed with screws.

Section 3. Optimization of slurry.

The optimization of the semi-solid slurry was carried out using the cell shown in Figure S2. For the optimization, two plates of W were used as blocking electrodes while separator was not placed in between. In this configuration, one can evaluate the electrical conductivity of the slurries from electrochemical impedance spectroscopy (Figure S3a

and S3b) using the equivalent circuit developed for mixed ionic and electric conductors (Figure S3c). For the semi-solid electrode of 72 % electrode porosity, the electrical conductivity was in the order of 1.5 Ohm cm² (for 2-mm thick electrode with 2 interfaces current collector – electrode).



Figure S3. (**a**) Impedance spectroscopy for semi-solid mixtures with different porosities and (**b**) magnification of (**a**). (**c**) Illustration of the determination of the electrical conductivity from the EIS data using the equivalent circuit developed for mixed ionic and electric conductors.

Section 4. Negative electrode (anode) for high areal capacities.

When demonstrating high areal capacities in Al-ion batteries, the negative electrode may become the limiting side. Figure S4 shows that the use of Al foil or Al mesh is not adequate for high areal capacities and it is necessary to combine Al foil and mesh to exceed 10 mAh cm⁻² to ensure that the positive electrode is the limiting one.



Figure S4. (a) Galvanostatic oxidation and reduction of Al in symmetric cell for Al foil (black) Al mesh (red) and Al Foil +Al mesh (blue).

Section 5. Utilization rate of active material

Figures S5 and S6 show a comparison of specific capacities obtained when using



conventional and semi-solid cathodes at different current densities.

Figure S5. Specific capacity *vs* current density for conventional and semi-solid Al-ion Batteries with 1, 2 and 4 mm of thickness.



Figure S6. Areal capacity *vs* current density for conventional and semi-solid Al-ion Batteries with 1, 2 and 4 mm of thickness.

Section 6. Estimation of ratio between effective diffusion coefficients.

The diffusion coefficients of a conventional and of a semi-solid Al-ion battery were compared by means of electrochemical impedance spectroscopy (EIS). For that, batteries using conventional cathode and semi-solid cathode with a thickness of 4-mm were assembled to ensure mass transport limitation through the electrode. Both batteries were charged at 50% of the State of Charge and then, EIS measurements were conducted from 10 mHz to 200 kHz with an amplitude of 10 mV. In the low frequency region (Warburg region), the effective diffusion of the ions through the electrode can be obtained. The

effective diffusion coefficient (D) of the species can be calculated by following equations

9:

$$Z_r = R_{ct} + R_s + \sigma \,\omega^{-\frac{1}{2}} \tag{1}$$

$$n - \frac{\frac{2}{2} \frac{2}{R_{*}^{2} T}}{2A^{2} n^{4} F^{4} C_{i}^{2} \sigma^{2}}$$
(2)

As it can be seen in the equation (1), plotting Z_r as function of the $\omega^{-\frac{1}{2}}$ a linear trend can be achieved. The slope of this line in low frequencies is the Warburg coefficient, σ , in Ω s^{-1/2}. This value was calculated for batteries using a conventional cathode (σ_{conv}) and a semi-solid cathode (σ_{semi}).

Once the Warburg coefficient is calculated, the ratio between the two diffusion coefficient $(D_{conv} \text{ and } D_{semi})$ can be obtained since the rest the parameters such as the gas constant (R), the area (A), the absolute temperature (T), the number of electrons (n), the Faraday constant (F) and the concentration of the ions (C_i) can be considered the same for both batteries. Therefore, the ratio between the diffusion coefficients is calculated as:

$$\frac{D_{semi}}{D_{conv}} = \frac{\sigma_{conv}^2}{\sigma_{semi}^2} = \frac{0.9814^2}{0.7332^2} = 1.79$$

Section 7. Molar ratio of the electrolyte

Since the mass of the graphite was 1.09 g and the practical specific capacity of graphite was 51 mAh g⁻¹, the total charge stored in the devices was 55.6 mAh

C_g= 1.09 g * 51 mAh g⁻¹ = 55.6 mAh

Taking into account that the percentage of the electrolyte in weight was 46.4% and the mass of the graphite was 1 g, the mass of the electrolyte was = 0.95g. Furthermore, 1 mL of electrolyte is added to the separator to soak it. The volume added was ~1 mL, which corresponded to *ca.* 1.4 g. Then, the total mass of the electrolyte was 2.35g. Based on the calculation developed by Kravchyk⁶, the capacity of the electrolyte for r=1.5 is 24 mAh

g⁻¹. Therefore, the anode capacity was:

 C_a = 2.35 g * 24 mAh g⁻¹ = 56.4 mAh

If lower amount of electrolyte is to be used in the separators, the higher molar ratio (1.5 -

2.0) will be required.

Section 8. Energy density and specific energy calculation

The energy density and specific energy were calculating assuming a thickness for the Al and W current collectors of 50 μ m and a specific capacity of 80 and 50 mAh g⁻¹ for conventional and semi-solid electrodes, respectively. An electrode porosity of 45 vol% and 58 vol% are used for conventional and semi-solid AlBs, respectively. It should be noted that 1 mAh cm⁻² is considered as state-of-the-art value for conventional AlBs while a value of 7 mAh cm⁻² is demonstrated in this work.

Section 9. Cost breakdown for conventional and semi-solid electrodes.

The contributions of the battery components to the overall cost are given in Table S2. First of all, it should be noted that the overall cost is reduced by 80 %. While the current collector is the main contributors to the cost for both conventional and semi-solid electrodes, the contribution of the electrolyte increases for semi-solid electrodes. Thus, the semi-solid based battery is expected to benefit from the significant advances in the production cost of ionic liquids.

Battery Component	Cost (%). Conventional electrdoes. 1 mAh cm ⁻²	Cost (%). Semi-solid electrode. 7 mAh cm ⁻²
Electrolyte	14.2	26.9
Graphite	3.8	18.1
Binder	0.2	0
Separator	6.7	4.5
Positive Current Collector (W)	72.9	49.1
Al Foil (Negative Current Collector)	2	1.3

Table S2. Cost breakdown for a battery using conventional and semi-solid electrode

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