Supporting Information

Polyacrylonitrile separator for high-performance aluminum batteries with improved interface stability

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Table S1 reports the comparison of the thickness and of the chemical stability against the EMIMCl:$AlCl_3$ electrolyte of some of the available commercial separator for batteries application. The measurements evidence that the investigated separators, representative of the most conventionally used for the realization of commercial batteries as well as for research purpose are not compatible with the high reactive electrolyte used in aluminum batteries.

Table S1 Comparison of the thickness, aspect and mass loss of membranes with different nature, from different suppliers, before and after full immersion in EMIMCl:$AlCl_3$ electrolyte.

Reference	Specification (measurement)				
	Composition	Thickness (µm)	Mass Loss (%)	Aspect	
				Before	After
Sep 1	PP	23	20		
Sep 2	Glass fiber	195	1.2		
Sep 3	Cellulose/PAN	30	11		
Sep 4	PE/PP + PVA	25	0.0		
Sep 5	PP (3D)	32	50		
Sep 6	Polyimide	22	7.4		

Figure S1 reports the SEM pictures of two PP separators (top views), having different morphology, obtained from different manufacturers: #1 (left) and #5 (right). The higher porosity of the separator #5 leads to a larger amount of polymer dissolution.

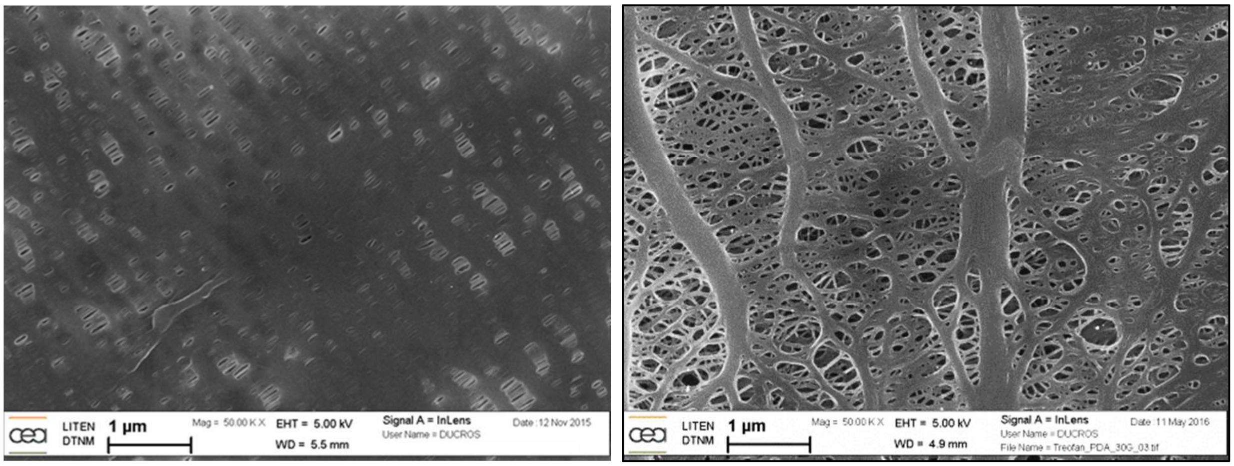
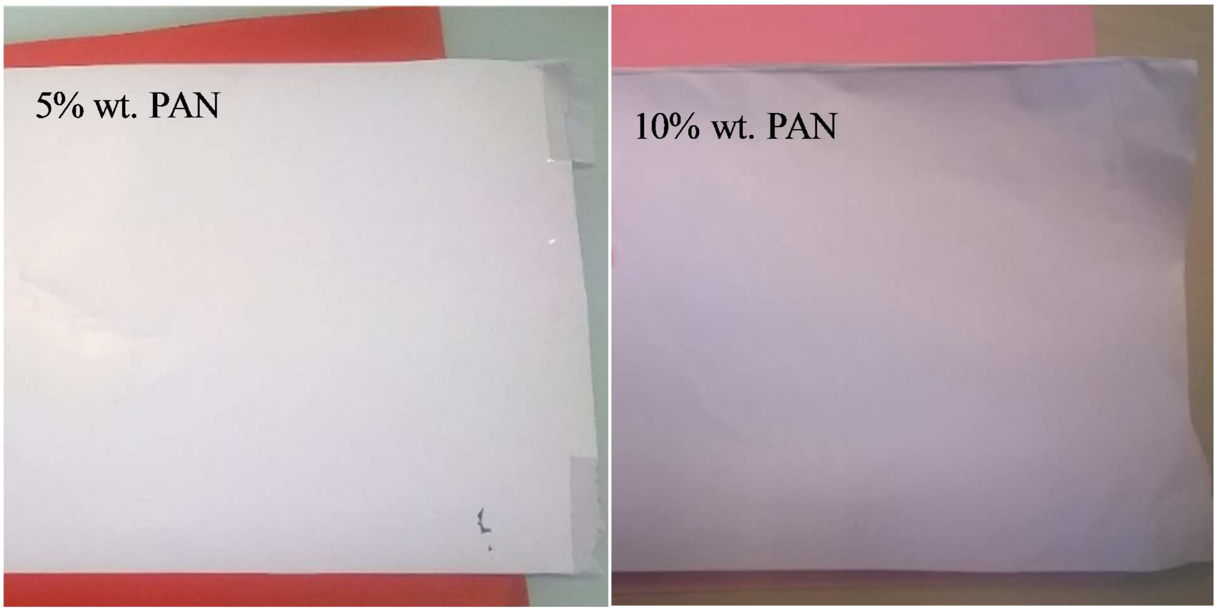


Figure S1 SEM pictures of two PP separators (top views), having different morphology, obtained from different manufacturers: #1 (left) and #5 (right).

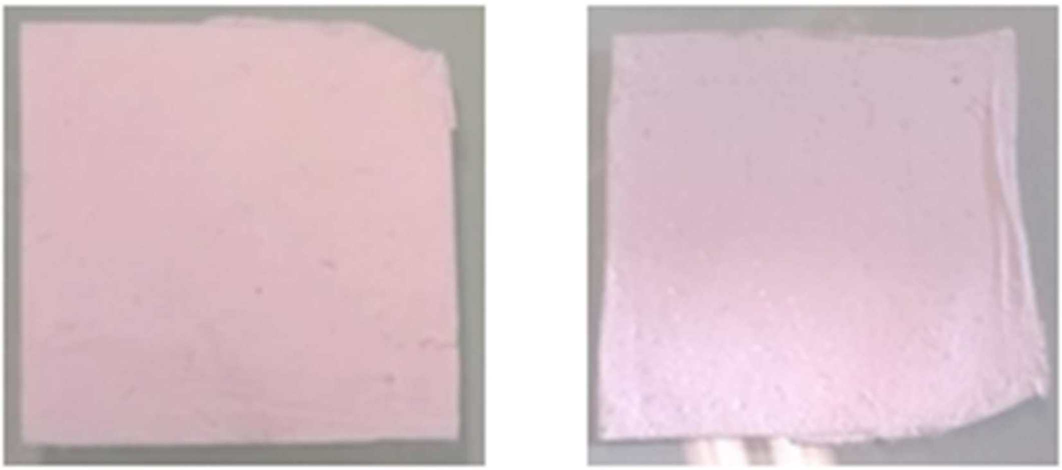
Figure S2 show the photographic images of the membrane obtained employing the 5% wt. PAN solution (figure S2a) and the 10 % wt. PAN solution (figure S2b), in both cases a 30 cm x 20 cm homogeneous membranes were obtained.



(a) (b)

Figure S2. Picture of PAN electrospun membranes prepared from 5% (a) and 10% (b) PAN solutions in DMF.

Figure S3 shows the photographic image of a 16 cm^2 square PAN membranes before (figure S3a) and after heat treatment (figure S3b) at 150°C during 1 hour under air.



(a) (b)

Figure S3. Picture of the 16 cm^2 square PAN membranes before ***(a)*** and after ***(b)*** heat treatment at 150°C during 1 hour under air.

Table S2 reports the values of the shrinkage of the PAN membrane in comparison with commercial polyolefin (PP monolayer and PP-PE-PP trilayers) separators.

Table S2. Shrinkage (%) of the membranes after heat treatment under air, during 1h, at 90°C and 150°C

Membrane	**90°C/1h, air**	**150°C/1h, air**
PP monolayered	2.5%	2.5%
PP-PE-PP trilayered	2.5%	2.5%
10% PAN electrospun	5%	5%

Table S3 reports the Gurley values obtained for different membranes (#1, #2, #3) and compared to the PAN electrospun membrane.

Table S3 Gurley values obtained for different membranes, compared to the PAN electrospun membrane

Membrane	**Gurley value (sec)**
PP monolayer (#1)	622
Glass fibers (#2)	1.3
Cellulose/PAN fibers (#3)	2.8
10% PAN electrospun	5.7

Figure S4 reports the cycling behavior of six Al/graphite cells, three employing the PAN separator and three employing the glass fiber separator. Galvanostatic cycling was performed using a current density of 25 mA g^{-1}. The measurements performed to have a statistical evaluation on the delivered capacity of the two systems, clearly confirm that in average the cells employing the PAN separator deliver a slightly higher capacity in respect to those employing the glass fiber separator.

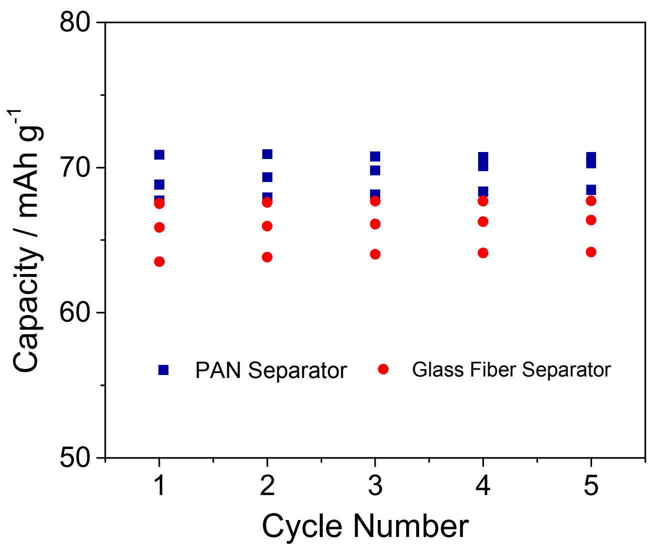
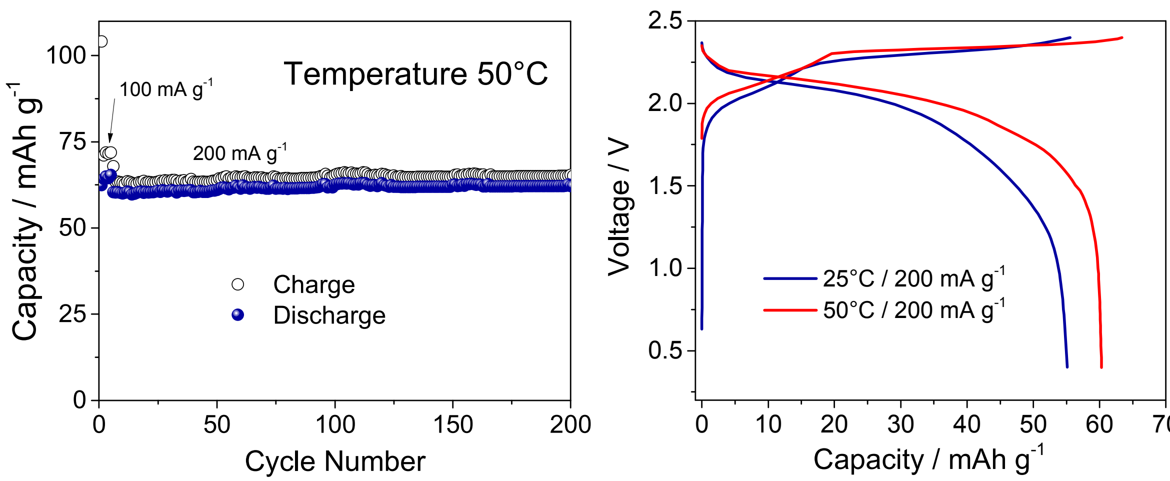


Figure S4. Cycling behavior of Al/EMINCl:$AlCl_3$/PG cells galvanostatically measured at 25 mA g^{-1}, employing the PAN separator (blue squares) and the Whatman glass fibers separator (red circles).

Figure S5a reports the cycling behavior of the Al/EMIMCl:$AlCl_3$/PG cell employing the PAN separator galvanostatically cycled at 100 mA g^{-1} for the first five cycles and at 200 mA g^{-1} for the following. The measurement clearly evidences the stability of the investigated separator at mid-high temperature operation. **Figure S5b** reports the comparison of the voltage signature of the Al/EMIMCl:$AlCl_3$/PG cell employing the PAN separator galvanostatically cycled at 200 mA g^{-1} at a temperature of 25°C (blue line) and at 50°C (red line).



(a) (b)

Figure S5 **(a)** Cycling behavior of the Al/EMIMCl:$AlCl_3$/PG cell employing the PAN separator galvanostatically cycled at 100 mA g^{-1} for the first five cycles and at 200 mA g^{-1} for the following. **(b)** Comparison of the voltage signatures of the Al/EMIMCl:$AlCl_3$/PG cell employing the PAN separator at a current of 200 mA g-1 at 25°C (blue line) and at 50°C (red line) of temperature.