Supplementary Information (SI) for Sustainable Energy & Fuels.

Supplementary data

Experimental Section

Materials:

20 µm thick natural graphite foil with a graphite loading of 4.5 mg cm^{-2} (Heepani tools store, Alibaba, China) was cut into Ø = 9 mm discs and washed with isopropanol to remove the surface impurities followed by vacuum drying at 105°C under vacuum using a self-built Schlenk-line apparatus and subsequently moved into a glovebox (UniLabPro, $H_2O/O_2 < 0.1$ ppm, MBraun, Garching, Germany) for further use. The graphite foil did not contain any binder materials and has a porosity <2%. Therefore, the absolute mass of graphite foil was considered as the active mass for calculations. Al foil (thickness of 200 µm, 99.5%, ChemPUR), and Mo rod (Ø = 10 mm, 99.999%, HMW Hauner, Röttenbach, Germany) were thoroughly washed with isopropanol and dried before the use. Glass fiber membrane GF/A (260 µm in thickness, Whatman™/Cytiva, Freiburg, Germany) and PES membrane (160 µm in thickness , Sartorius Stedim Biotech GmbH, Göttingen, Germany) were cut into φ 10 mm discs and dried at 105°C under vacuum using a self-built Schlenk-line apparatus and subsequently moved into the glovebox for further use. EMIMCl:$AlCl_3$ of molar ratio 1:1.5, 1:1.8 and 1:2.0 (98% purity, Iolitec, Heilbronn, Germany) electrolytes were stored and used as received inside the glovebox. Dimethyl carbonate (DMC) (98% purity, Iolitec, Heilbronn, Germany) were used as received.

Physical characterisation of separator:

The porosities of GF/A and PES separators were measured using n-butanol absorption method. The mass of the separators was measured before and after immersion in n-butanol for 1 hour. The porosities of the separators were calculated by the following equation:

$$Porosity\ (\%) = \frac{Ma - Mb}{\rho V} \text{ x } 100\%$$

where Mb and Ma are the weight of the separators before and after soaking in n-butanol for 1 hour, respectively; before weighing the samples, the excess n-butanol on the surface was wiped clean; ρ is the density of n-butanol; V is the volume of the sample.

Pore size distribution was measured by capillary flow porometry by 3P Instruments GmbH & Co. KG. All samples were used without prior preparation. Samples were placed on a wired mesh disc support and covered with a masking adapter to generate an area of 25mm in diameter. Samples were wetted using the liquid Galwick (Surface tension 15.9 dyn/cm). All calculations were conducted with a tortuosity factor of 0.715.

The contact angle of Millipore water on the PES surface was evaluated by the sessile drop method using a contact angle goniometer OCA15Pro instrument (DataPhysics Instruments GmbH) in ambient air at room temperature. A total of 10 µL of Millipore water was dropped carefully through the 0.5 mm OD needle tip onto the sample surface. The image was taken at the 0 seconds of the liquid drop formed on the PES.

The EMIMCl:$AlCl_3$ electrolyte uptake of the separator was obtained by measuring the weight of separators before and after soaking in the electrolyte for 12 h and then calculated using the following equation:

$$Electrolyte\ uptake\ (\%) = \frac{Wa - Wb}{Wb} \text{ x } 100\%$$

where Wb and Wa are the weights of the separators before and after soaking in the liquid electrolyte, respectively. Before measuring the mass of the separator with electrolyte, the excess electrolyte on the surface of GF and PES membranes was wiped off using a polymer weighing boat. The electrolyte uptake was measured for 5 samples and the average is reported.

N/P ratio calculation

Molar ratio of EMIMCl/$AlCl_3$	Electrolyte capacity (mAh g^{-1})
1:1.5	28.99
1:1.8	41.59
1:2.0	48.63

Electrolyte requirement based on capacity of graphite loading

- Mass loading of graphite – 4.5 mg cm^{-2}
- Average specific capacity of graphite foil – 80 mAh g^{-1}
- Average mass of Ø 9 mm graphite foil – 2.7 mg
- Average absolute capacity of Ø 9 mm graphite foil – 0.216 mAh

Molar ratio of EMIMCl/$AlCl_3$	Required quantity of electrolyte for Ø 9 mm graphite foil (P) (in g)	Electrolyte uptake by GFA (N) (in g)	N/P ratio with GF separator	Electrolyte uptake by PES (N) (in g)	N/P ratio with PES separator
1:1.5	0.00746	0.042	5.63	0.01095	1.47
1:1.8	0.00520	0.0428	8.23	0.011	2.12
1:2.0	0.00445	0.0439	9.87	0.0114	2.56

To examine the thermal stability, the thermal shrinkage ratio was calculated according to the following equation:

$$Thermal\ shrinkage\ (\%) = \frac{Aa - Ab}{Aa} \text{ x } 100\%$$

where Aa and Ab are the areas of the separator before and after thermal treatment at 200°C for 2h. Additionally the thermal stability of the PES membrane was analysed using thermogravimetric analysis (TGA) (Netzsch, Jupiter STH 4) with a constant flow of air up to 900°C at a heating rate of 10°C per minute.

For the cross-section analyses, the samples were frozen in liquid nitrogen for 5 min, then taken out and pulled from both ends with tweezers until the membrane broke in two without any damage in the pore structure. The observation of the surface and cross-sectional morphology of the PES membrane was obtained using a FESEM (4100 Hitachi, Tokyo, Japan) at 10 mm WD and 10 kV power. The cycled aluminium electrode, PES and GF separator were removed from the cells inside the glovebox and were washed thoroughly with DMC solution and was later dried to remove the residual electrolyte for further FESEM characterisation.

Raman spectra of PES membrane were measured with a confocal Raman microscope (InVia Reflex, Renishaw, Pliezhausen, Germany). The laser beam (532 nm) was focused through a 20× objective lens (DM 2500, Leica, Mannheim, Germany) with ~1 mm spot size. A single spectrum consisted of 20 accumulated scans with an acquisition time of 20 s each. The background signal was subtracted using the baseline correction mode. Prior to the Raman analysis of PES membrane with electrolyte, the samples were washed thoroughly with DMC solution inside the glovebox and was later dried to remove the residual electrolyte. The Al anode after long-term cycling was removed.

Cell fabrication

The test cells with 2-electrodes made of PTFE (Swagelok®) with an internal diameter of φ 10 mm were used. All the cells were assembled in an argon-filled glovebox. For Al-graphite full cells, Al foil (φ 10 mm) was used as the anode and graphite electrode (φ 9 mm) was used as the cathode. Mo rods (φ 10 mm) were used as current collectors. 1 layer of GF/A or PES separator soaked with EMIMCl:$AlCl_3$ was used as the separator and no additional electrolyte was added to the cell.

Electrochemical measurements

Galvanostatic cycling experiments were conducted using a BioLogic BCS-810 battery testing system (Seyssinet-Pariset, France). The rate capability of the cells was evaluated at varying current densities ranging from 0.1 to 1 A g^{-1} within a potential window of 0.40 V to 2.40 V. For self-discharge characterization, cells were charged at 0.1 A g^{-1} to 2.40 V, then left in open-circuit conditions for durations up to 24 hours, followed by discharging at 0.1 A g^{-1} to 0.4 V. Each self-discharge cycle was followed by a regular charge-discharge cycle before the next self-discharge test. Long-term cyclic stability tests were conducted at a constant discharging current density of 1 A g^{-1} for 100 cycles, with the first 50 cycles charged at 1 A g^{-1} and the subsequent 50 cycles at 0.1 A g^{-1}. All experiments were performed at room temperature, and specific capacities were normalized to the mass of graphite.

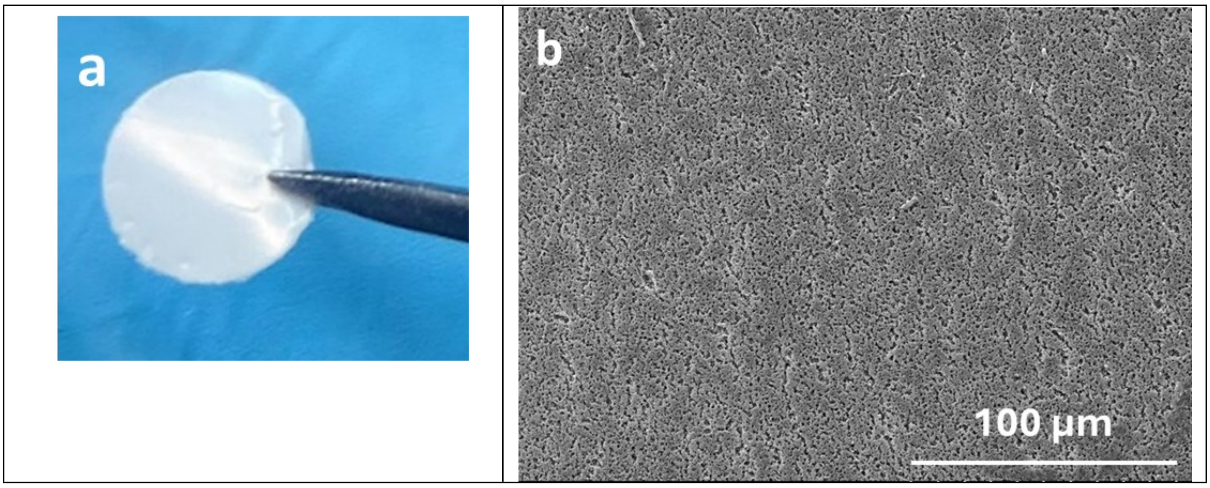

Figure S1: Image of PES separator after 7 days of soaking in 1:2 EMIMCl:$AlCl_3$

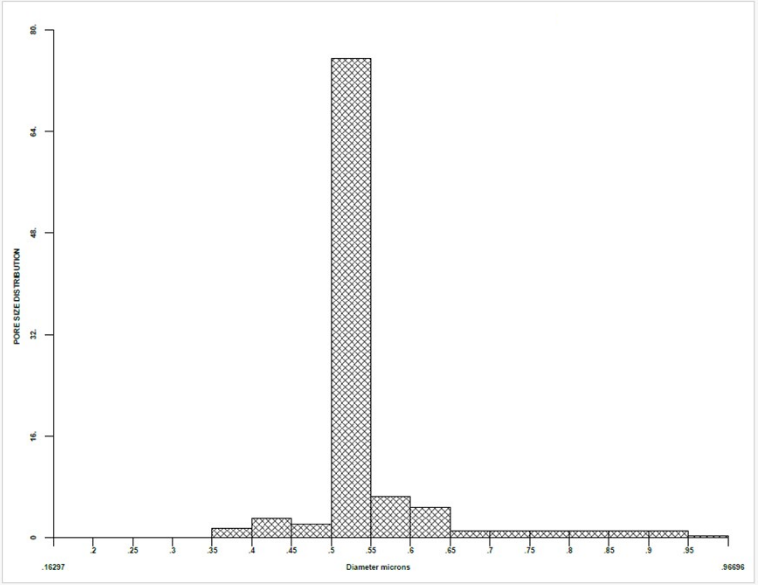

Figure S2: Pore size distribution of PES membrane measured by capillary porometry

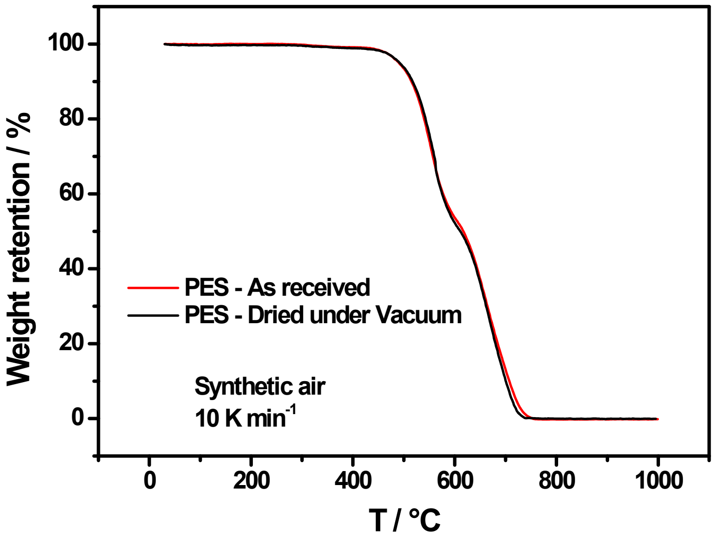

Figure S3: Thermogravimetric analysis of PES separator upto 1000°C under synthetic air

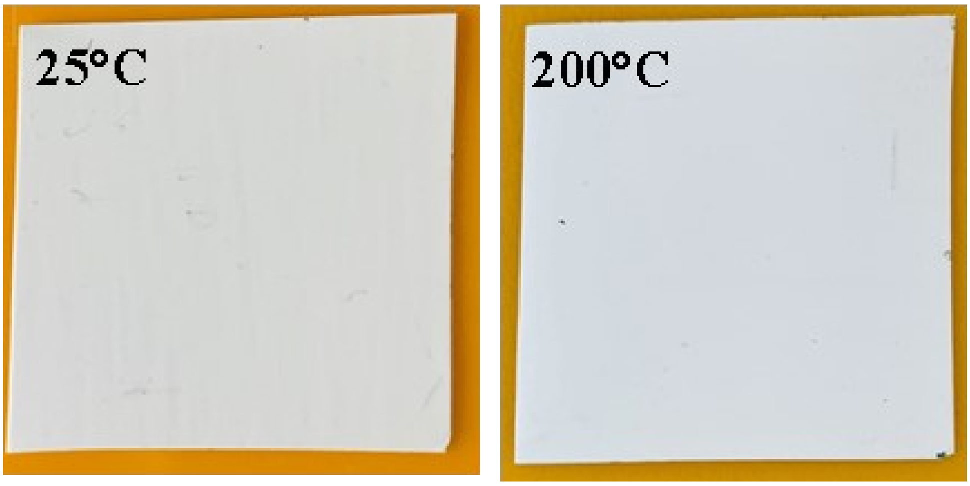

Figure S4: PES separator before and after shrinkage test at 200°C for 2h

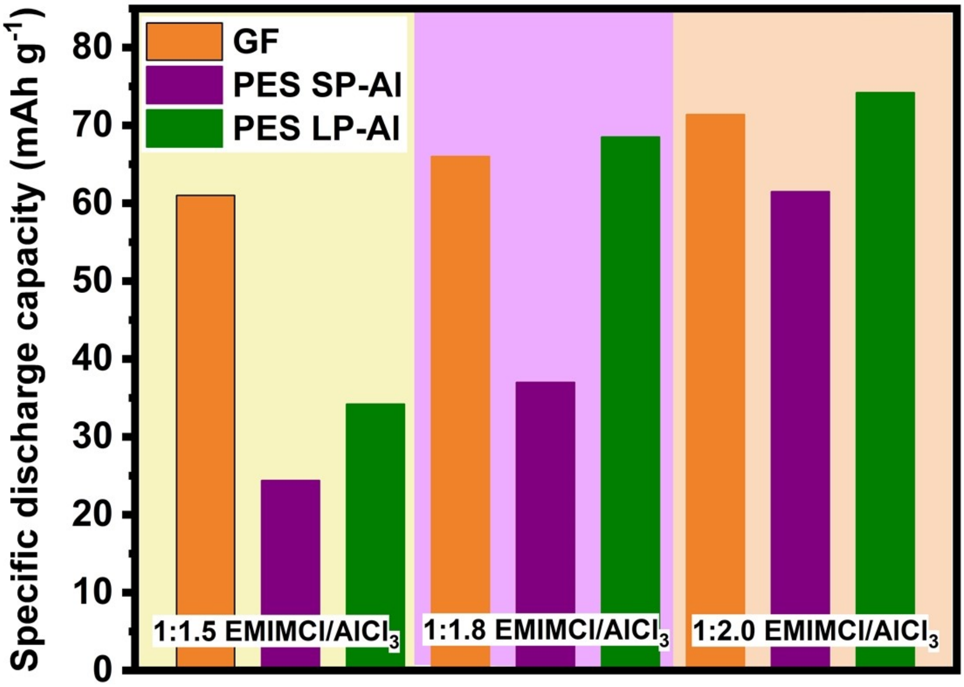

Figure S5: Influence of separator and molar ratio of EMIMCl/AlCl$_3$ on the specific capacity at a discharging rate of 1 A g^{-1} after charging at 1 A g^{-1}

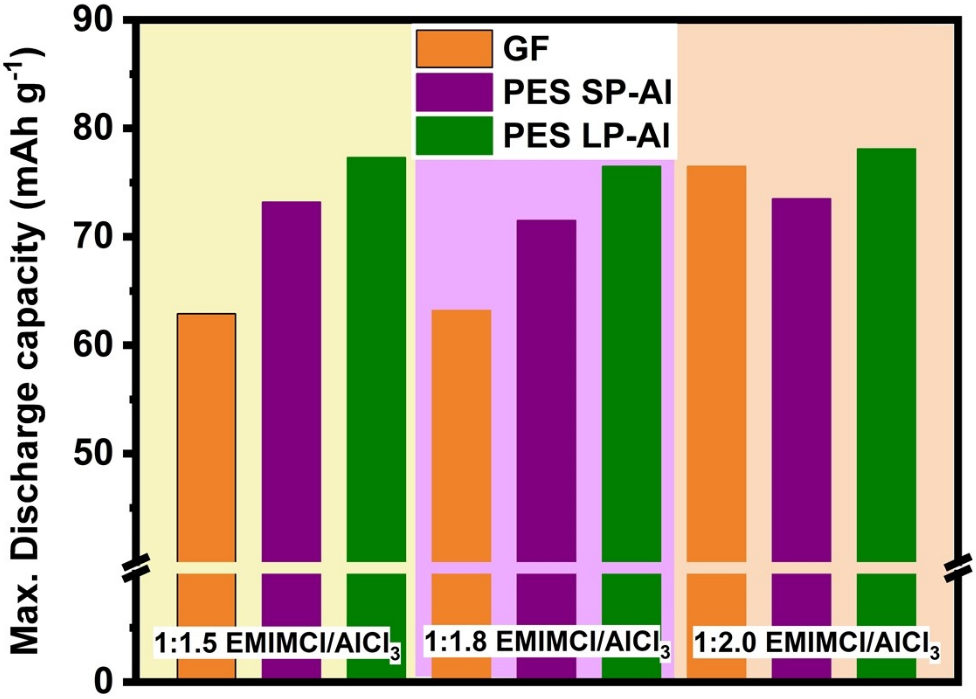

Figure S6: Influence of separator and molar ratio of EMIMCl/AlCl$_3$ on the specific capacity at a discharging rate of 1 A g^{-1} after slow charging at 0.1 A g^{-1}

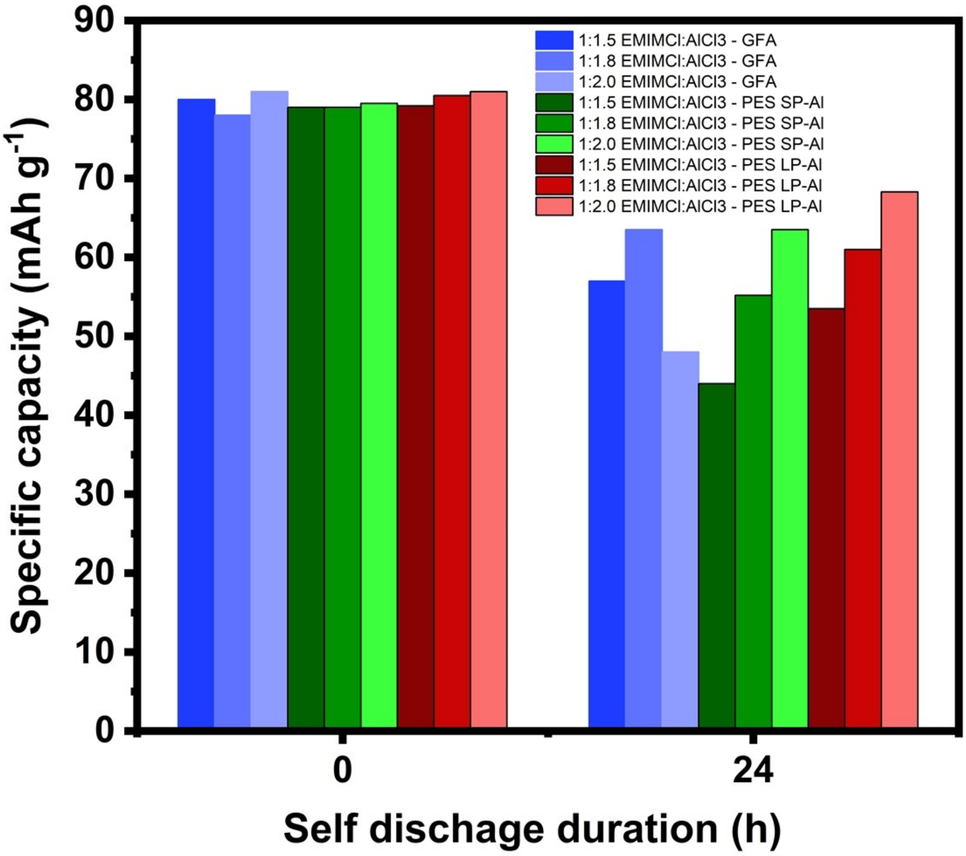

Figure S7: Influence of separator and molar ratio of EMIMCl/$AlCl_3$ on the specific capacity obtained at 0.1 A g^{-1} after a self-discharge duration of 24 hours

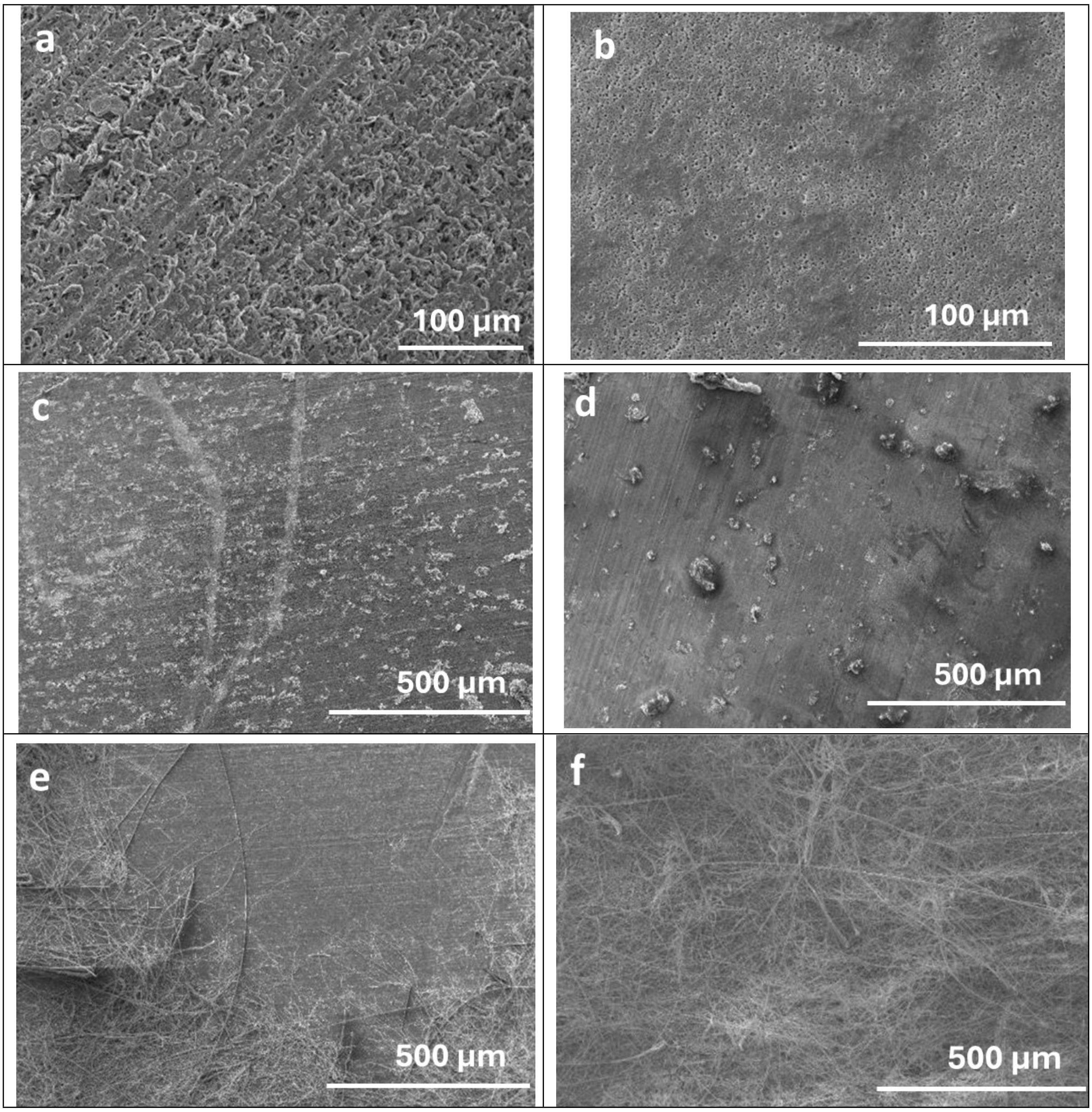

Figure S8: SEM images of PES separator on Al side in a) LP-Al, b) SP-Al. Al anode with c) LP-Al PES, d) SP-Al PES, (e-f) GF separator after long-term cycling for 100 cycles with 1:2 EMIMCl/$AlCl_3$