

Supplementary Information

Experimental Section

WET Process Poly(acrylonitrile) PAN-LiClO₄ 50wt% and acrylonitrile-methyl acrylate copolymer latex AMAC-LiTFSI 30wt% films preparation.

The preparation of the PAN and LiClO₄ electrolyte-based solutions is done in two steps. First, N-Methyl-2-pyrrolidone (NMP) is added to the previously weighed polymer in a vial. The quantities of each component are measured to obtain 10wt% PAN in NMP. The mixture is stirred at least overnight to ensure complete dissolution of the polymer in the solvent.

Then, LiClO₄ (battery grade, dry, 99.99% trace metals basis – Sigma Aldrich) is added to the polymer solution. The LiClO₄ being very hygroscopic, in order to be precise, the salt is weighed in a vial inside a *MBRAUN*® glove box with argon atmosphere (<0.1ppm H₂O ; 15-30 ppm O₂). The quantity of salt is weighted accordingly to obtain 50wt% LiClO₄ to PAN ratio. Then, the previously prepared polymer solution is added to the LiClO₄, outside the glovebox. The resulting mix is stirred during an extra night to ensure the dissociation of the salt. The final solution is translucent and moderately viscous.

To obtain a self-supporting film, the polymer electrolyte solution is evenly casted on a glass substrate with a doctor blade using a *Gardco*® *Automatic drawdown machine II DP-8301*. Afterwards, the film is dried for 1-hour at 110°C at atmospheric pressure, then under a -28mmHg vacuum for 24 hours at the same temperature.

Once dry, the film is taken out of the oven and peeled off the glass support using a rectangular razor blade. Subsequently, the self-supported film is transferred to a glovebox within less than 10 minutes in contact with air. The film's thickness is 120-200 μm .

The AMAC-LiTFSI 30wt% film preparation follows the same steps as the WET process described for the PAN-LiClO₄ system. The AMAC solution in NMP is prepared at 15wt%. The quantity of LiTFSI is weighted accordingly to obtain 30wt% LiTFSI to AMAC ratio. The resulting film thickness is 120-200 μm .

DRY (solvent-free) process PEO-LiTFSI 24.5wt% film preparation.

Firstly, high molecular weight (PEO average MW 5 000 000, Sigma Aldrich) is mixed with equal amounts of low molecular weight (PEO average MW 20 000, Fluka Chemie AG, Buchs, Switzerland) in a closed internal mixer Brabender® (30 mL volume of the working chamber) at 170 °C \pm 5 °C, until a homogeneous molten polymer blend is obtained, then the 24.5 wt% of LiTFSI (Shenzhen Capchem Technology) are added gradually until a homogeneous blend is obtained. The latter is then processed in a hydraulic press and cooled between steel plates. The resulting film thickness is 140-160 μm .

The procedure used to obtain the mixture with the PEO was chosen to represent manufacturing conditions. The following articles demonstrate that the polymer can be affected by the mixing procedure: L. Froboese, L. Groffmann, F. Monsees, L. Helmers, T. Loellhoeffel, and A. Kwade, *J. Electrochem. Soc.*, 2020, **167**, 020558.

P. Malik, M. Castro, and C. Carrot, *Polym. Degrad. Stab.*, 2006, **91**, 634-630

Measuring the membranes' residual water content.

The residual moisture content of membranes is determined using a BrookField AMETEK® Computrac® Vapor Pro® XL specific moisture analyser that is calibrated and verified by measuring water content of a 1 μ L microcapillary tube Drummond Microcaps®. On one hand, this system correlates to the Karl-Fischer titration, but it is more user-friendly and does not require usage of reagents. On the other hand, it is also more accurate than determining water content by measuring the loss of total weight of the sample, since it employs a water-specific polymer capacitor relative humidity sensor based on change in its dielectric properties. In practice, the instrument's oven heats the polymer sample to volatilise residual water, then, the carrier gas vehicles the steam to the polymer capacitor moisture sensor. We use argon for the carrier gas (95 mL/min), it flows through an inline Drierite® desiccator before reaching the instrument to ensure its dryness. The samples are weighted in screw caps vials with septa inside an argon-filled glovebox, and they can be tested without being exposed to air. In order to start a measurement, the instrument first equilibrates the relative humidity of the carrier gas for correcting purposes. Then, the sample-containing vial is purged with the carrier gas for 30s to ensure that any headspace moisture is eliminated from the vial. This causes the detected-water rate to drop to 0 μ g/s. Afterwards, the sample is heated to 200°C for LiTFSI containing membranes. (150°C is used for LiClO₄ containing membranes, because higher temperatures caused the samples to combust yielding aberrant excessively high detected water quantities). Similarly to the Karl-Fischer titration method, the instrument measures the water rate count and stops the measurement once the rate reaches 0.10 μ g/s. Each type of sample is tested five times. The method presents a relative systematic error of about 5%.

Determining ionic conductivities using complex impedance spectroscopy.

Four-point impedance measurements are performed using a Biologic MTZ-35 high frequency impedance analyser or an SP300. The 1cm in diameter SPE membranes are sandwiched between two stainless steel current collectors and sealed in a controlled environment sample holder inside an Argon glovebox. The samples are heated and tested at temperatures ranging from 40 to 80 and down to 30 °C (with a measure every 10°C) using an intermediate temperature system. All samples are thermally equilibrated for a minimum of 3 hours at every temperature.

Controlled water-doping of SPE membranes.

Different SPE membranes of 1cm in diameter are cut from the same region of the mother film and are sealed individually under an argon atmosphere in 20mL headspace vials. 10mL of distilled water are sealed in a 20mL headspace vial and heated at 190°C for 20 minutes. 4mL of the headspace water atmosphere are collected using a syringe and are injected into the sample-containing vials. The same volume of vapour is injected into all the SPE samples. Diffusion is left for 1h and then the vials are opened in the glovebox in order to get rid of any potential residual water atmosphere. Every type of samples is tested for water-content and ionic conductivity parallelly.

Water content of samples influencing the activation energy.

The activation energies of different samples have been calculated from the conductivity data assuming a VTF-type behaviour. The Vogel temperature (T_0) was calculated as $T_0 = T_g - 50K$, where T_g is the glass transition temperature of the polymer electrolyte. As observed in **figures S1; S2 and S3**, activation energy seems to decrease with water content.

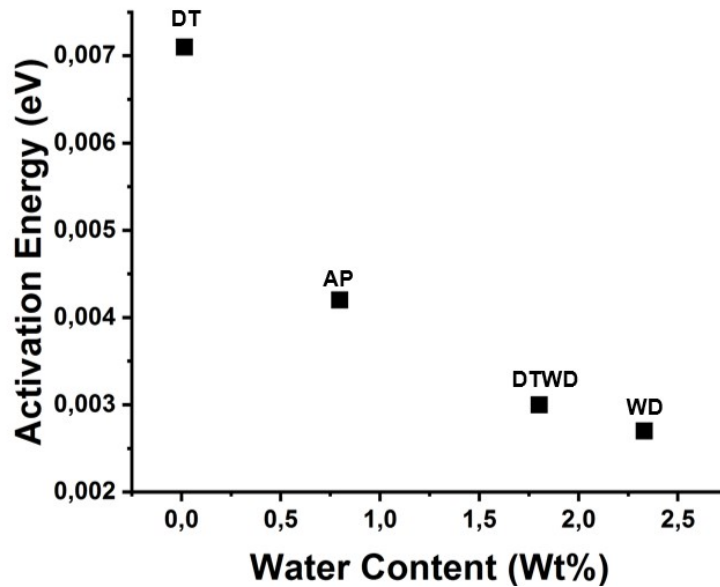


Figure S1. Decreasing activation energy with increased water contents in PAN-LiClO₄.

In **figure S2**, the portions of the conductivity curve above and below 60°C have been separated. Indeed, above 60°C the activation energy seems more stable with respect to the variation of water content. That could imply that above 60°C the mobility of the PEO chains already offers optimal conduction conditions regardless of water content. However, below 60°C, water contributes to the conduction mechanism as shown by the decrease in activation energy between the dryer samples (AP and DT) and the more hydrated samples (DTWD and WD).

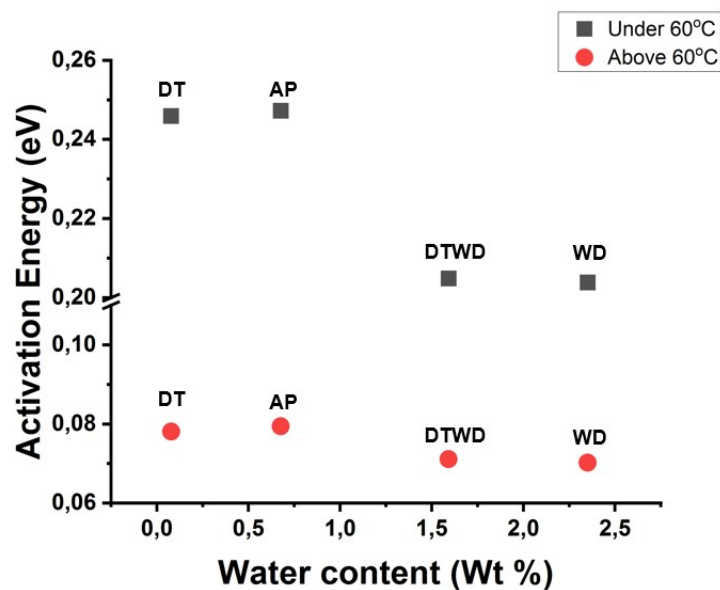


Figure S2. Decreasing activation energy with increased water contents in PEO-LiTFSI.

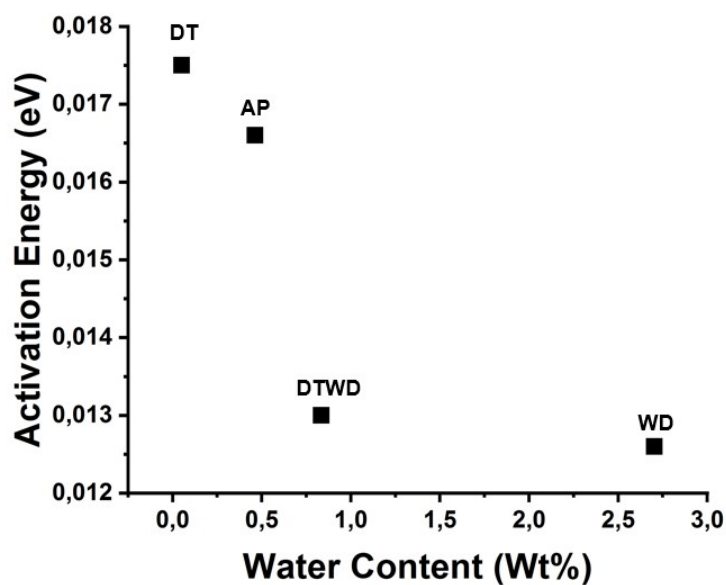


Figure S3. Decreasing activation energy with increased water contents in AMAC-LiTFSI.

The trends seem to be system-specific, however, in all cases, drying a sample increases the activation energy and water-doping it decreases the E_a . The fact that the process is observed, regardless of the polymer/salt combination, is quite interesting because it confirms that water plays

a role in the ionic conduction mechanism. Considering the complexity of the latter, we'd rather not advance any further interpretations of these data, but it is worth reminding that the choice of T_0 must be carefully considered in order to represent a physical parameter of the system. Until further understanding of these systems is achieved, these trends present an obvious correlation between the increase of water content and the decrease of activation energy.

Supporting tables

Table S1.a – Conductivity data and error of PAN-LiClO₄ 50wt% - AP

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
80	$3,63 \times 10^{-4}$	$7,46 \times 10^{-5}$
70	$2,66 \times 10^{-4}$	$7,73 \times 10^{-5}$
60	$1,78 \times 10^{-4}$	$1,10 \times 10^{-4}$
50	$1,14 \times 10^{-4}$	$9,47 \times 10^{-5}$
40	$6,82 \times 10^{-5}$	$6,72 \times 10^{-5}$
30	$3,70 \times 10^{-5}$	$4,81 \times 10^{-5}$

Table S1.b – Conductivity data and error of PAN-LiClO₄ 50wt% - DT

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
80	$3,13 \times 10^{-6}$	$4,85 \times 10^{-6}$
70	$7,37 \times 10^{-7}$	$1,16 \times 10^{-6}$
60	$2,04 \times 10^{-7}$	$3,24 \times 10^{-7}$
50	$2,74 \times 10^{-8}$	$4,04 \times 10^{-8}$
40	$3,85 \times 10^{-9}$	$5,08 \times 10^{-9}$
30	$5,26 \times 10^{-10}$	$5,59 \times 10^{-10}$

Table S1.c – Conductivity data and error of PAN-LiClO₄ 50wt% - DTWD

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
80	1,44x10 ⁻⁴	1,46x10 ⁻⁴
70	1,31x10 ⁻⁴	1,23x10 ⁻⁴
60	1,16x10 ⁻⁴	1,13x10 ⁻⁴
50	7,56x10 ⁻⁵	7,16x10 ⁻⁵
40	5,21x10 ⁻⁵	5,19x10 ⁻⁵
30	1,32x10 ⁻⁵	1,45x10 ⁻⁵

Table S1.d – Conductivity data and error of PAN-LiClO₄ 50wt% - WD

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
80	5,69x10 ⁻⁴	2,34x10 ⁻⁴
70	4,68x10 ⁻⁴	1,53x10 ⁻⁴
60	3,54x10 ⁻⁴	1,30x10 ⁻⁴
50	2,45x10 ⁻⁴	1,08x10 ⁻⁴
40	1,57x10 ⁻⁴	8,30x10 ⁻⁵
30	9,47x10 ⁻⁵	5,77x10 ⁻⁵

All average conductivities presented in **Table S1** are calculated from triplicated measurements. Some error bars have been omitted from **Figure 2.a** for clarity purposes.

Table S2.a – Conductivity data and error of AMAC-LiTFSI 30wt% - AP

Temperature [°C]	Ionic conductivity [S/cm]
80	$1,17 \times 10^{-5}$
70	$5,68 \times 10^{-6}$
60	$2,37 \times 10^{-6}$
50	$8,48 \times 10^{-7}$
40	$2,65 \times 10^{-7}$
30	$7,06 \times 10^{-8}$

Table S2.b – Conductivity data and error of AMAC-LiTFSI 30wt% - DT

Temperature [°C]	Ionic conductivity [S/cm]
80	$7,55 \times 10^{-8}$
70	$1,84 \times 10^{-8}$
60	$4,79 \times 10^{-9}$
50	$1,32 \times 10^{-9}$
40	$3,89 \times 10^{-10}$
30	$8,97 \times 10^{-11}$

Table S2.c – Conductivity data and error of AMAC-LiTFSI 30wt% - DTWD

Temperature [°C]	Ionic conductivity [S/cm]
80	$2,12 \times 10^{-7}$
70	$5,88 \times 10^{-8}$
60	$1,58 \times 10^{-8}$
50	$4,69 \times 10^{-9}$
40	$1,49 \times 10^{-9}$
30	$5,12 \times 10^{-10}$

Table S2.d – Conductivity data and error of AMAC-LiTFSI 30wt% - WD

Temperature [°C]	Ionic conductivity [S/cm]
80	$1,64 \times 10^{-5}$
70	$8,09 \times 10^{-6}$
60	$3,50 \times 10^{-6}$
50	$1,32 \times 10^{-6}$
40	$4,23 \times 10^{-7}$

All conductivity data presented in **Table S2** has been acquired during the same day.

Table S3.a – Conductivity data and error of PEO-LiTFSI 24.5wt% - AP

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
40	$1,46 \times 10^{-5}$	$3,18 \times 10^{-6}$
50	$9,15 \times 10^{-5}$	$5,62 \times 10^{-6}$
60	$4,39 \times 10^{-4}$	$1,63 \times 10^{-5}$
70	$6,60 \times 10^{-4}$	$3,95 \times 10^{-5}$
80	$9,97 \times 10^{-4}$	$1,03 \times 10^{-4}$

Table S3.b – Conductivity data and error of PEO-LiTFSI 24.5wt% - DT

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
40	$1,67 \times 10^{-5}$	$9,89 \times 10^{-6}$
50	$1,00 \times 10^{-4}$	$5,22 \times 10^{-5}$
60	$4,93 \times 10^{-4}$	$8,04 \times 10^{-5}$
70	$7,56 \times 10^{-4}$	$8,72 \times 10^{-5}$
80	$1,10 \times 10^{-3}$	$8,90 \times 10^{-5}$

Table S3.c – Conductivity data and error of PEO-LiTFSI 24.5wt% - DTWD

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
40	$4,53 \times 10^{-5}$	$2,34 \times 10^{-5}$
50	$1,97 \times 10^{-4}$	$7,70 \times 10^{-5}$
60	$7,61 \times 10^{-4}$	$1,65 \times 10^{-4}$
70	$1,13 \times 10^{-3}$	$2,22 \times 10^{-4}$
80	$1,58 \times 10^{-3}$	$2,89 \times 10^{-4}$

Table S3.d – Conductivity data and error of PEO-LiTFSI 24.5wt% - WD

Temperature [°C]	Average ionic conductivity [S/cm]	Standard deviation [S/cm]
40	$3,15 \times 10^{-5}$	$1,20 \times 10^{-5}$
50	$1,59 \times 10^{-4}$	$1,35 \times 10^{-5}$
60	$5,18 \times 10^{-4}$	$9,60 \times 10^{-5}$
70	$7,48 \times 10^{-4}$	$2,15 \times 10^{-4}$
80	$1,07 \times 10^{-3}$	$2,91 \times 10^{-4}$

All average conductivities presented in **Table S3** are calculated from triplicated measurements.