# Experimental report

25/03/2025

**Proposal:** **6-07-134** **Council:** 4/2024

**Title:** Insights into the ionic diffusion of three-components solid electrolytes based on polyvinylidene fluoride, Metal-organic frameworks and ioni

**Research area:** Materials

**This proposal is a new proposal**

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**Samples:** PVDF-TrFe-CFE
PVDF-TrFe-CFE/UiO-66
PVDF-TrFe-CFE//[Dema][TfO]
PVDF-TrFE-CFE/UiO-66@[Dema][TfO]

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN16B | 3 | 2 | 24/06/2024 | 26/06/2024 |

## Abstract:

Solid Polymer electrolytes (SPEs) are currently a hot topic on the energy storage subject. After detailed investigations we have chosen Polyvinylidene fluoride (PVDF) as polymeric matrix for our SPEs composites. The incorporation of ionic liquids (IL) and Metal-organic frameworks (MOFs) into the SPEs had shown a great improvement on the composite properties. Interestingly, the ternary system (PVDF/MOF/IL) revealed surprisingly good results comparing to the simpler system of PVDF/IL only. We assume that the MOF¿s cavities allow a higher IL loading into the composite, and improves also the anion capture that consequently eases the pathway to cation, improving the SPEs performance. Physic-chemical (including SANS characterization) and then battery charge/discharge cycling tests have been applied to validate this assumption. Nevertheless, we could not conclude which mechanism is taking place and contributing to this performance improvement. Thus, with QENS technique is aimed to understand the influence of each component on the polymer dynamic behaviour of the complex ternary system, important contribution on the ionic mobility throughout the membrane.

# Report exp 6-07-134 IN16B: Insights into the ionic diffusion of three-components solid electrolytes based on polyvinylidene fluoride, Metal-organic frameworks and ionic liquids

## 1. Scientific background

The transition from the fossil fuel-based society to circular and green energy one relies today in the development of new generation battery technologies for stationary storage and transportation purposes. Although electrode components of energy storage systems have been extensively studied for many years, the research on the separator and electrolyte layer of the batteries is still in a nascent stage. For instance, the transition from classic liquid electrolytes to all solid-state batteries (SSBs) based on solid electrolytes is considered today a key objective to increase the safety (i.e. leakage, toxicity, flammability) while improving the performance of classic battery modules preventing the Li-dendrites propagation after mid to long-terms operation. As expected when moving from a liquid to solid ionic/lithium conductor systems, the first of the challenges to overcome is to approach the ionic conductivity and Li-effective mobility of the SSE to the classic liquid ones. In parallel, the electrochemical affinity, surface compatibility and the mechanic proprieties of the SSE have to be balanced until reaching a good compromise between then and the final performance of the cell. Here is where the combination of polymeric membranes with ionic liquids (ILs) can make the difference to the development of Solid Polymer Electrolytes (SPE).

## 2.- Scientific case

Among the myriad of polymeric scaffolds that can be employed for this end, polyvinylidene fluoride (PVDF) polymer stands out for its chemical and mechanical resistance, and easy processability as dense or porous membranes. The semi crystalline and amorphous domains within the PVDF~~,~~ as well as glass transition temperature (Tg), enable some degree of motion of polymeric chains that promotes ionic mobility, but still the best conductivity values obtained in the system are far for its technical application as SPE.[1] And this handicap has been easily solved by integrating ILs (e.g. Emin-TFSI) containing lithium ions (i.e. Li-TFSI) into the PVDF dense solid electrolytes~~.~~ Their chemical versatility, high ionic conductivity and negligible vapour pressure have made them the ideal green liquid electrolyte component to integrate into SPE systems. In addition, ILs do interfere with the PVDF matrix, being able to change from their electroactive crystalline phases to the overall structure of the membrane. In fact, although some part of the IL integrated into the PVDF matrix remains homogeneously dispersed into the polymer, other part is usually concentrated as IL-drops confined into the PVDF-scaffold. Thus, in order to solve this handicap, porous nanoparticles of different materials, as zeolites and Metal-Organic Framework (MOFs), have been employed as a filler into PVDF/IL SPEs. These porous particles increase the maximum IL-loading that can be integrated into the PVDF solid electrolytes, and also favours an outstandingly homogeneous dispersion of the ILs along the solid electrolyte. All in all, even if the overall ionic conductivity values decrease when engineering PVDF/IL/MOF three-components SPEs, the effective Li-transport (i.e. transference number) and the rate and stability performance of the battery increases significantly[2].

Among the multiple PVDF, IL and MOF combinations already studied by our team, the ones combining dense PVDF membranes with the UiO-66 zirconium MOF, and Diethylmethylammonium triflate [Dema][TfO] ionic liquid are the ones with the best performing, both in terms of ionic conduction and battery cycling (capacity at different rates, stability among others). The weight ratio between the components have been screened until the maximum performance has been achieved. All in all, by comparing the response of different three-component SPE already studied by our team, it is still unclear what are the mechanisms that led to this enhanced Li-transport of three-component PVDF/IL/MOF - SPE in comparison to two component PVDF/IL ones. The morphological, physic-chemical, impedance spectroscopy, solid-NMR, SANS and electrochemical analyses acquired throughout PhD work of the main proposer of the proposal (Vera Macedo) suggest that: (I) the IL has a deep impact in the mobility of PVDF polymeric chains and its nanostructure (as determined by SANS), and in parallel, (II) that the MOF acts as an active component of the system, not only storing IL, but fixing their anions, and then, promoting the generation of effective Li-transport paths across the solid electrolyte. At this close to the end point of our study, we believe that applying QENS measurements of our two and three-component SPEs could help to understood the mobility of the individual components of our systems before and after their integration into the final solid electrolyte.

## 4. Objective of the experiment

QENS measurements will help to correlate the underlying molecular dynamics of each component when integrated into the SPE, and correlate it with the values of the ionic conductivity obtained from electrochemical impedance spectroscopy, the nanostructure of the SPE, and the dielectric properties of the SPE when applied in a battery.

## 5.Experimental part

We performed temperature-dependent QENS study of 3 composites of PVDF/UiO-66@[Dema][TfO] (polymer matrix with MOF loaded with ionic liquid), that were produced in different curing processes, and the respective neat PVDF matrix, produced in the same condition, which give a total of 6 samples. It aided to understand the influence of the curing process on the dynamic behaviours of these polymer and composite materials. First, we started by analysing the composite that in previous studies have showed more promising properties in the scope of solid electrolyte for all-solid-state batteries applications, followed by the respective neat matrix. The QENS analysis was performed in the same way to the other samples. We requested time to do elastic and inelastic combined scans at RT, and 333K, (which temperature is usually verified a great improvement on ionic conductivity), on each of the component's matrix and the ternary composite to identify the dynamical transitions and dynamics of interest within the timescale of the IN16B spectrometer. Despite the fact of not being possible to clearly see the influence of the applied voltage, it was detected differences on dynamic behaviour between the neat and respective composite samples, and with the increasing of temperature (from RT to 333K) as well. This behaviour was observed in each curing process samples set (SA_Composite and SA_PVDF, SB_Composite and SB_PVDF, SC_Composite and SC_PVDF). In Figure 1.a) and b) it can be observed for the case of SB_Composite and SB_PVDF samples.

Interestingly, while previous studies have shown that differences in sample production methods significantly impact physicochemical properties and cyclability during galvanostatic analysis, the influence of the different curing processes on the dynamic of the polymer chains was not as clearly observed. (Figure 1.c) and d)). This indicates that the diffusion mechanism behind the $Li^+$ transport in this case study may not be as much related with motion of polymer chains or IL's species.

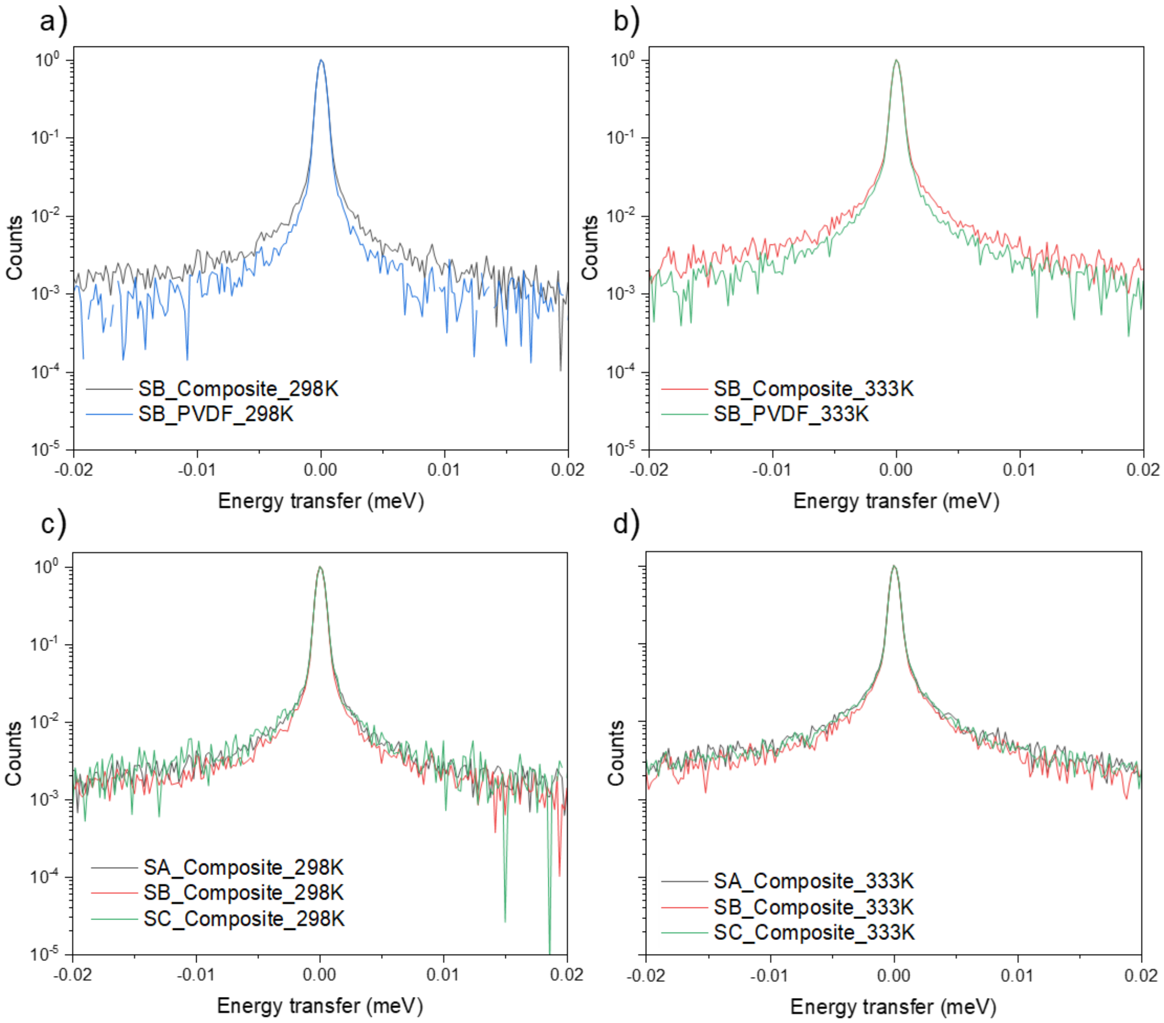

*Figure 1. QENS spectrum of a) SB_Composite and SB_PVDF at 298K, b) SB_Composite and SB_PVDF at 333K, c) all sample composites at 298K, and d) all composites at 333K.*

The next step will involve a more detailed analysis and fit of the obtained data, to better correlate it with the previous results and then incorporate it into the article manuscript.

**Scientific Responsibilities** Vera Macedo is the responsible for materials preparation and electrochemical characterization, and Viktor Petrenko responsible and expert in neutron scattering characterization.

## 6. References

1. Barbosa JC et al. Journal of Power Sources 2023;585, 233630, 2. Urgoiti-Rodriguez M et al. Frontiers in chemistry 2022;10, 995063-995063,