AAPG2024	**2POLI**		PRC.
Coordinated by:	Trang PHAN	48 months	607 658 €
Axe H9 – Une énergie durable, propre, sûre et efficace – CES05			

NanoPorous Polymer electrolytes for high energy Lithium batteries

Table of content

Summary table of persons involved in the project:

Partner	Name	First name	Current position	Role & responsibilities in the project (4 lines max)	Involvement (person.month) in project's total duration
ICR Aix-Marseille Univ	*PHAN*	*Trang*	*MCF*	*Coordinator* *Tasks 1 & 2* *Block copolymers synthesis and characterization*	*18*
	GIGMES	*Didier*	*DR CNRS*	*Participant (partner 1), Task 1* *Block copolymers synthesis*	*4*
	ROLLET	*Marion*	*IE*	*Participant (partner 1), Task 1* *Polymers characterization*	*6*
ICR Aix-Marseille Univ LLB – CEA Saclay	*To be recruited (ANR funding)*		*PhD student 1*	*Tasks 1 & 2* *Copolymer synthesis and characterization*	*36*
IEM Montpellier Univ	*AISSOU*	*Karim*	*CR CNRS*	*Scientific leader of partner 2* *Task 1*	*14*
	VAN DER LEE	*Arie*	*IE CNRS*	*GISAXS measurements*	*4*
	To be recruited (ANR funding)		*PhD student 2*	*Self-assembly of DBCP chains into NPEs and electrolyte loading*	*36*
	To be recruited (ANR funding)		*M. Sc. Student*	*Phase behavior of DBCP membranes and study of their ion and water transports*	*6*
LLB - CEA Saclay	*ZANOTTI*	*Jean-Marc*	*DR CEA*	*Scientific leader of partner 3* *Task 2*	*5*
LEPMI Grenoble-Alpes Univ.	*BOUCHET*	*Renaud*	*Pr*	*Scientific leader of partner 4* *Tasks 2 & 3,* electrochemical characterization of NPEs	*10*
	SOUDANT	*Priscilla*	*IE*	*Task 2* *Diffusion coefficients by PFG-NMR*	*4*
	MERMOUX	*Michel*	*DR CNRS*	*Task 2 & 3* *Raman characterization*	*6*
	To be recruited (ANR funding)		*PhD student 3*	Tasks 2 & 3	*36*

I. Proposal's context, positioning and objectives

a. Context, objectives and research hypothesis

The production capacity of lithium-ion batteries (LIBs) has risen tenfold over the past decades.[1] This demand is expected to continue growing rapidly over the next 10-30 years, driven mainly by the fast development of electric vehicles (EVs) market.[2] Indeed, according to the International Energy Agency publication, there was more than 26 million electric and plug-in hybrid cars on the road around the world at the end of 2022, an increase of 60% in one year, and this trend continues growing up year after year.[3] Meanwhile, numerous joint ventures involving major original equipment manufacturers are launching a hundred of Gigafactory projects over the world to secure the future electric transportation market that will be highly depending on the future battery innovations.[4] In this context, developing next-generation batteries with higher performance (*i.e.*, energy (350-400Wh/kg, 1000-1200Wh/L), safety, lifetime (2000 cycles) and low cost) is essential for the EV market, and could also create a short-haul electric aviation industry.[5] Unfortunately, the liquid electrolytes based on organic carbonate solvents used in today's LIBs are highly flammable leading to string safety issues especially when coming to large battery pack. In addition, the graphite negative electrode with a relatively low specific capacity (372 mAh g^{-1}) is also limiting the density energy for improving further performance of the state-of-the-art LIBs.[6] In this regard, lithium metal batteries (LMBs) associated high energy positive electrode materials and solid electrolytes are considered as the most promising approach to circumvent both the safety issues and low energy density of current LIB technologies. Indeed, lithium metal is considered as the ultimate negative electrode due to its high theoretical capacity (3860 mAh g^{-1}) and low redox potential (-3,04 V *vs* standard hydrogen electrode).[7] On the other hand, solid polymer electrolytes (SPEs) notably those based on poly(ethylene oxide) (PEO) are very interesting due to their attractive advantages including light-weight, good elasticity, flexibility, and ease of thin film processing. However, the low intrinsic ionic conductivity (σ) of PEO-Li salt complexes ($\sigma \approx 10^{-6}$ S cm^{-1} at 25°C) limits their practical use at room temperature (RT).[8] The migration mechanism of Li-ion (Li^+) in PEO relies on Li^+ hopping attempts between adjacent free volumes, which depends mainly on the polymer chain dynamics, and are strongly lower than the motions in liquid electrolyte, that explains the poor conductivity. The second key obstacle for the commercialization of lithium metal-based secondary batteries is the safety problem caused by the so-called lithium dendrites growth. Li-dendrites are electrode surface protrusions that grow during Li platting (*i.e.* during the charge of the battery) on the electrode's flat surface. After 70 years of research, the mechanism of lithium dendrites formation is always under intense debate. Nevertheless, it is admitted that the regulation of cations and anions activities at the surface region of Li metal anode is of great importance for enabling a uniform Li deposition. According to Chazalviel's model,[9] in a binary electrolyte, above a critical current density (*i.e.*, Sand's current density) the anion depletion to zero leads a severe space-charge region and electric field at the metallic electrode/electrolyte interface that trigger the nucleation of Li dendrites. Thus, Li^+ single ion conducting electrolytes, which prevents the formation of gradient of concentration, represent one of the most important strategies to inhibit the lithium dendrite growth. To immobilize the anions, we have previously showed the concept through two effective strategies *i)* the use of a block copolymer (BCP) system composed of PEO as ionic conductive block and lithium poly(styrene sulfonyl(trifluoromethane sulfonyl) imide) as both reinforcing phase and Li^+ source where the anion is grafted to the polymer backbone,[10,11] and *ii)* the use of macro-anions where anions were grafted onto polyhedral oligomeric silsesquioxane (POSS) molecules in a liquid electrolyte.[12] In these studies, the resulting lithium transport number (t_{Li^+}) was around 0.85 and σ was 10^{-5} S cm^{-1} at 60°C in polymer electrolyte and 1.9 10^{-4} S cm^{-1} at RT in the liquid electrolyte with macro-anions.

In a recent perspective paper, M. Armand *et al.*[13] highlighted that SPEs with improved **electrochemical stabilities and ionic conductivities, particularly cation-only conductivities**, will continue to be a desirable solution for the development of future solid-state LMBs (SSLMBs). In line with this guideline, enhancing the Li^+ conductivity of SPEs is essential to improve the rate-capability of SSLMBs and for this, Li^+ should move independently of the polymer. This so-called decoupled system cannot be obtained for Li salt/polymer complexes because of the chemical interactions constantly occurring between ions and the polymer chains. Therefore, in a decoupled superionic system, the influence of polymers on the motion of Li^+ should be minimized, and the ionicity of salt should be maximized. So far, the search for **a superionic Li^+-conducting salt with low melting-point** is still ongoing and represents a great challenge for the electrolyte research community.[14] From another perspective, one may also replace typical neutral polyether/polyesters with charged polysalts to regulate the ion-ion interactions, thereby achieving decoupled SPE systems.[15] It was demonstrated that due to the nanometric confinement effects, affecting particularly collective phenomena (including the crystallization, high conductivity, high t_{Li}^+, and exceptional ability to stabilize the Li deposition), have been achieved in nanoporous hybrid electrolytes based on nanometric γ-Al_2O_3 ceramic filled with conventional liquid electrolytes.[16] However, ceramic electrolytes, having a low adhesion to electrode-active materials, are too brittle to compensate the electrode volume changes during cycling and are also difficult to manufacture, which hinders their practical use. On the other hand, Sharon *et al.*[17] have tracked the electrodeposition of silver ions dissolved in PEO electrolyte confined inside channels formed by lithographic defined line-and-space polystyrene patterns They observed the suppression of silver dendrite growth can be achieved if the dimensions of conducting channels are lower than 70 nm. Their study aims to introduce a generalizable platform for a direct characterization of electrodeposited metal morphologies in well-defined, multiphase nanostructured electrolytes by imaging.

In line with those challenges, we propose in the present research project to manufacture and study the structure-property relationships of **original nanoporous polymer electrolytes (NPEs)** specially designed for high energy LMBs. These NPEs will be created by infusing small electrolyte molecules (*i.e.*, carbonate-based electrolyte, ionic liquid electrolyte or oligomer electrolyte) within voided double gyroid (DG) or vertically-aligned nanochannel-forming BCP membranes. To produce such freestanding and nanostructured membranes endowed with voided channels, BCP chains including a degradable block will be specifically devised in the ***2POLI*** project. Such nanoporous polymer electrolytes will address the following requirements to unlock some of the current LMB technology bottlenecks: **1**) **High ionic conductivity close to that of a liquid electrolyte** (*i.e.* $>10^{-3}$ S cm^{-1} at RT) because the electrostatic interactions between ions and pores surface will facilitate the ion transport. **2**) **Increase of t_{Li}^+ close to 1** because a liquid electrolyte confined in the nanopores of the polymer matrix with even modest surface charge can function as an ion rectifier (impeding transport of anions with the same charge as the pore surface), yielding high t_{Li}^+. **3**) **Improve the electrodeposition of lithium** according to the works of Tu *et al.*[16] and Sharon *et al.*[17], as well as provide a new generation of nanoporous functional polymer membranes with high wettability compared to the conventional polyolefin-based macroporous membranes.

The objective of the *2POLI* project is thus the efficient design of quasi solid-state electrolyte membranes that answer all the performance requirements of LMBs such as $\sigma_{RT} \approx 10^{-3}$ S cm^{-1}, $t_{Li}^+ \geq 0.8$, EWS ≈ 4.5 – 5 V and cyclability ≥ 1000 cycles.

b. Position of the project as it relates to the state of the art

S. Vorrey and D. Teeters were among the first to study the confinement of PEO/Li triflate polymer electrolytes in nanopores of track-etched polycarbonate filtration membranes, and observed an increase of the ionic conductivity (σ) when the pore size decreases from 400 nm to 30 nm.[18] The highest σ was obtained for the membrane with pores diameters around 30 nm (2.43 10^{-4} S cm^{-1} at RT), which is almost two orders of magnitude higher than that of an unconfined PEO electrolyte film having the same composition. According to these authors, the σ increase is due to the combination of an enhanced interfacial conduction, a favorable polymer chains orientation in the pores and a reduction of the polymer crystallinity. Recently, Wan *et al.*[19] have obtained good electrochemical performance from ultrathin solid polymer composite electrolyte endowed with aligned nanoporous host structure. Instead of working with thick nanoporous membranes having small pores, these authors worked with a 8.6 μm thick nanoporous polyimide film having pores of 200 nm in diameter filled with a PEO/LiTFSI electrolyte. An enhanced σ of 2.3 10^{-4} S cm^{-1} at 30°C and good cycling performance up to 200 cycles at 60°C were reported for this nanoporous polymer electrolyte. Importantly, the common point of these two studies are the use of track-etched polymer membranes. Although, this technique allows tuning the pores size of polymer membranes, one cannot modulate neither the pore wall chemistry nor the pores density (generally lower than 15%) of nanoporous membranes. Conversely, the self-assembly of BCP chains offers a versatile platform to tailor the size and geometry of nanopores at large-scale as well as a great ability for selective functionalization of voided channels. Indeed, BCPs, composed of two or more thermodynamically incompatible polymer blocks with distinct physical and chemical properties covalently bonded together, repel each other, causing an accurate microphase-separation. This phase behavior, also known as the BCP self-assembly, leads to the formation of various nanostructures including lamellae, hexagonally close-packed cylinders, body-centered cubic packing of spheres, and double gyroid networks depending on the size and composition of BCP chains (see **Figure 1**). The well-defined structural arrangements of BCPs at mesoscale (2 to 50nm) make them excellent platforms to achieve nanoporous membranes by a selective removal of the minor block.[20] Note that nanoporous membranes derived from the BCP self-assembly are already used in separation-based membranes, nanotemplates, etched masks for catalysis, biomedicine and microelectronics applications.[21]

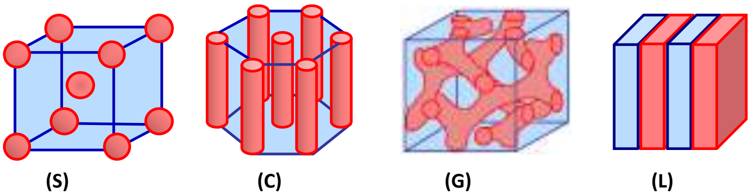


***Figure 1**: Schematic illustration of morphologies accessible from self-assembled AB-type BCP chains where nanodomains occupied the minority block are shown in red while the remaining space (i.e., the matrix in blue) is filled by the majority block. This includes spherical (S), cylindrical (C), double gyroid (G) and lamellar (L) structures.*[22]

To our knowledge, only one paper reported the use of nanoporous block copolymer membranes as lithium battery separators.[23] The BCP system used in this study was composed of a electrolytes-affinitive polysulfone block attached to a Li^+-solvating polyethylene glycol (PEG) block. Nanoporous membranes with PEG chains enriched along the pore walls were produced from these BCP chains by subjecting the films to a selective swelling process. The manufactured membranes were endowed with a 3D interconnected structure consisting of circular and elongated pores. The average pore width and BCP film thickness were approximatively of 30 nm and 22 μm, respectively. This membrane of 36.9 % of porosity exhibited ultrahigh electrolyte (hexafluorophosphate lithium at 1 mol L^{-1} in a mixture of solvent, EC/DMC 1:1 in volume) uptake up to 501% and prominent σ of 10.1 10^{-3} S cm^{-1} at RT. Although the thermal resistance of this membrane is as high as 150°C, the initial nanoporous structure disappears with the generation of dense structure above 125°C and the σ fall down to 2.7 10^{-4} S cm^{-1} at 125°C. Despite the good performance in terms of ionic conductivity and cycling of these nanoporous polymer electrolytes, the transference number was not measured as well as the multi-scale (from nm to μm) dynamics of confined species and their relationship with macroscopic properties were passed over. Note that these nanoporous BCP membranes have nanochannels in a higher areal density than that achievable by using a track-etching technique, which is crucial for facilitating ion conduction within SPEs. However, the presence of a 3D interconnected structure with obviously dead-end nanochannels (due to the presence of randomly distributed pores) makes that the ion transport is not optimized, since the tortuosity value strongly deviates from unity. In the contrary, track-etched membranes with vertically aligned pores provide low tortuosity for ion diffusion, but the porosity is rather low (#10%) and conductivity falls behind compared to scaffolds with randomly distributed pores. Therefore, the development of NPEs with vertically aligned ionic nanochannels in a high areal density (high porosity) is highly desired. **Degradable block copolymers (DBCPs) where one block could be selectively removed constitute an excellent platform to manufacture nanoporous membranes with well-defined morphology, high porosity, narrow pore size distributions, and abundant functional end-groups.**

According to the state of the art and our deep expertise in the domains of block copolymer engineering and self-assembly,[24–26] dynamic study of ionic species in confined medium[27], and SPEs for lithium battery technology,[10,28,29] there is a real need and great opportunities to develop brand-new family of functional nanoporous electrolyte membranes. These new electrolyte membranes are based on nanoporous polymer derived from the self-assembly of degradable block copolymers (DBCPs) filling with optimized liquid electrolyte to enhance energy, safety and cyclability of lithium batteries. Thus, **the main objective of the *2POLI* research project is to design multifunctional nanoporous polymer electrolytes that combine different antagonistic properties such as high ion transport at RT** ($\sigma > 10^{-4}$ S cm^{-1} and t_{Li}^+ close to 1)**, high mechanical strength, and stable electrodes-electrolyte interface**. We are confident that all these aspects can be achieved since:

- The nanoconfinement effect combined with low tortuosity of ion-conducting nanochannels will allow to reach high σ.
- The engineering of the pore surface chemistry and a customized liquid electrolyte will give access to high t_{Li}^+

- The preparation of elastomeric membranes with tunable cross-linking degree and glass transition temperature will compensate for the volume change of electrodes.

Therefore, by tuning the pore diameters (from 10 to 50 nm) with the size of the degradable block and properly choosing the pore wall chemistry as well as the lithium electrolyte nature, we are confident of finding the best combination for developing optimized NPEs. Here the trade-off between mechanical properties and high σ will be overcome through the manufacture of elastomeric membranes endowed with voided vertically aligned cylinders or DG nanochannels that will be subsequently filled with an adequate lithium electrolyte. The development of this research project will definitely lead to breakthroughs that will address the major challenges inherent in fabricating **safe and high performance LMBs**.

c. Methodology and risk management

2POLI is a multidisciplinary research project (48 months), which is divided into 3 main scientific tasks covering a broad expertise in organic and polymer chemistries, multiple physical characterization techniques, and particularly emphasizing electrical and electrochemical properties for the development of improved nanoporous polymer electrolytes suitable for LMBs. These three tasks are: **(1)** the design, elaboration and characterization of nanoporous polymer electrolyte membranes; **(2)** the physical characterization and ionic transport properties of these nanoporous electrolyte membranes; **(3)** the characterization of electrochemical properties of the best materials selected from task 1 and 2 feedbacks, and the construction of lab-scale battery prototypes. The success of the ***2POLI*** project thus requires partners with very complementary skills and expertises in the fields addressed in this research project. For this reason, a strongly multidisciplinary and internationally recognized consortium has been gathered comprising four academic laboratories: *Institut de Chimie Radicalaire* (**ICR, Marseille**), *Institut Européen des Membrances* (**IEM, Montpellier**), *Laboratoire Léon Brillouin* (**LLB, Grenoble**) and *Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces* (**LEPMI, Grenoble**); who have already worked together in several academic and industrial projects.

- **Task 1 (ICR, IEM): Design of degradable block copolymers and fabrication of NPEs.**

Task leaders: Trang Phan and Karim Aissou
Main participants: M. Rollet (ICR), D. Gigmes (ICR), A. Van der Lee (IEM), PhD student 1 (ICR-LLB) and PhD student 2 (IEM)
Duration: M1 – M36

This task, held at **ICR** and **IEM**, will be devoted to the preparation of nanoporous polymer electrolyte membranes made of AB-and ACB-type BCP chains enabling a selective removal of the A block. There are three main post-processing methods to generate nanoporous membranes derived from the BCP self-assembly, namely the selective removal, selective swelling and non-solvent- induced phase separation (NIPS).[30] Among them, the selective removal methods have several advantages, such as a well-defined pore morphology, tailor-made pore chemistry, and simple process flow. The essence of the selective removal is to destroy sensitive groups that are concentrated/located within the minor phase of the BCP films. The BCP systems with this ability are known as degradable block copolymers (DBCPs), and will be used in ***2POLI*** to manufacture NPEs. These DBCPs consist of sacrificial domains, enriched with sensitive groups, giving rise to voided nanochannels within the remaining polymer matrix forming the membrane skeleton.[21]

This task is divided in three sub-tasks which are focused on: *1)* the development of an advanced macromolecular engineering strategy to produce **tuneable-by-design AB-** or **ACB-type DBCPs** able to self-assemble into the desired morphology (*i.e.*, a cylindrical or DG nanostructure) where **A** and **B** are the sacrificial and matrix blocks, respectively, while **C** is a Li-salt block that brings Li^+ in the pore (after being filled with a polar solvent). In ***2POLI***; the nanochanels walls will be negatively charged thanks to grafted anions, making our original membranes will be ion selective, with a high cationic transport number (herein t_{Li}^+). It will also amplify the affinity and wetting of the membrane by polar solvents, and *2)* the fabrication of AB- and ACB-type BCP membranes endowed with voided DG or vertically-aligned nanochannels generated by the degradation of the sacrificial A block, and *3)* the loading of polar solvent with or without a lithium salt. Polar solvents studied in the ***2POLI*** project will be a carbonate as the reference but also phosphate and ionic liquid as well as a customized oligomer functionalized lithium salt. **Figure 2** illustrates the different fabrication steps to achieve original NPEs derived from the DBCP self-assembly.

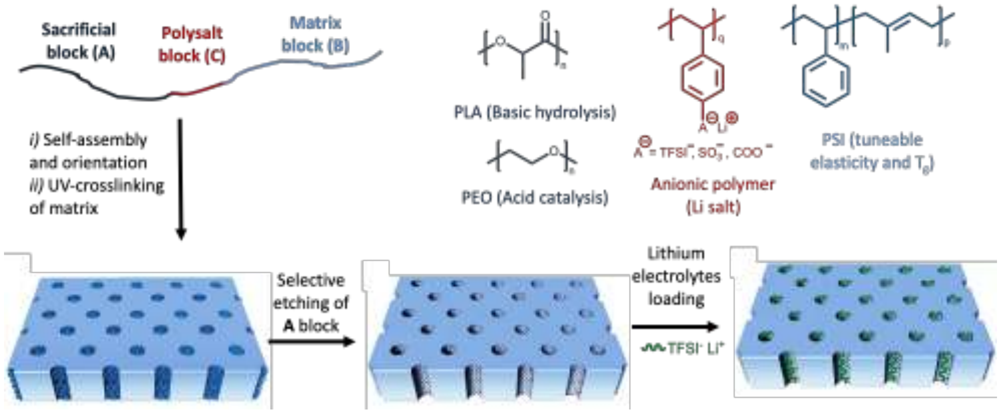
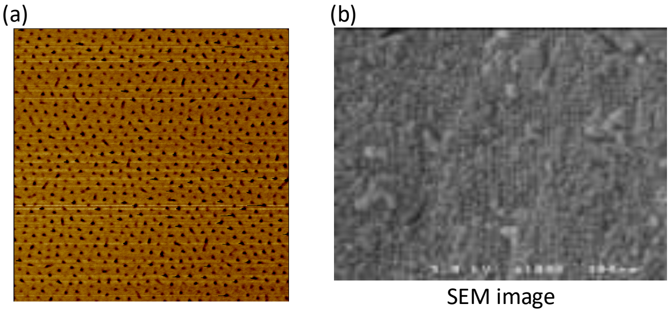


***Figure 2**: Schematic Illustration of the process route to manufacture NPEs.*

- Sub-task 1.1. Synthesis and characterization of degradable block copolymers

Objective: preparing a series of DBCPs with various chain length and functionalities in the aim to be target the desired morphologies.

Particular attention will be devoted to the design of **poly(isoprene-*co*-styrene)-based DBCP systems** enabling the selective removal of the **A** block. One of the key parameters determining the successful fabrication of NPEs is the creation of isoporous membranes having a high areal density of voided nanochannels, which could be only achieve by an efficient removal of **A** block. Thus, in ***2POLI*** we will consider two different sacrificial blocks made of amorphous polylactide (PLA) and semi-crystalline PEO chains. PLA is the most commonly used sacrificial block that can be hydrolyzed under mild alkaline conditions[31] while PEO can be removed by an acid catalyzed hydrolysis of ether bonds. The fabrication of nanoporous polystyrene (PS) membranes derived from the self-assembly of PS-*b*-PEO chains was already described in the literature.[32] In an internal study, we also elaborated with success nanoporous PS membranes formed by a PS-*b*-PEO-*b*-PS triblock copolymer containing 30 wt% of PEO. **Figure 3** shows the surface morphology of this PS-*b*-PEO-*b*-PS membrane before removal and after chemical etching of PEO block by HI.



(1µm x 1µm) AFM phase image

SEM image

***Figure 3**: Surface morphology of a PS-b-PEO-b-PS thin film (a) before and (b) after removal of 92 wt% of PEO blocks with a HI solution, leaving an isoporous PS membrane*

As the removal of PLA *via* a basic hydrolysis will let carboxylate groups on the pores surface of resulting nanoporous membranes, **PLA-based AB-type BCP** chains will be considered in ***2POLI.*** Conversely, PEO-based systems will have an **ACB-type BCP architecture** with a short **C** block consisting of an anionic polymer (**Figure 2**). The presence of anionic species ($TFSI^-$, SO_3^- or COO^-), and precisely the lithium polysalt, on the pores surface aims to facilitate the diffusion of ionic species and increase the transport number.

The **PLA-based AB-type BCP** chains will be synthesized in three steps as presented in **Figure 4**. First, hydroxyl-terminated poly(styrene-*co*-isoprene) (HO-PSI) will be obtained by copolymerization of styrene and isoprene monomers by nitroxide mediated polymerization (NMP) using alkoxyamine (**1**).[33] After purification, HO-PSI will be used as macroinitiator for the ring opening polymerization (ROP) of D, L-lactide units in the presence of $Sn(Oct)_2$ as catalyst.[34]

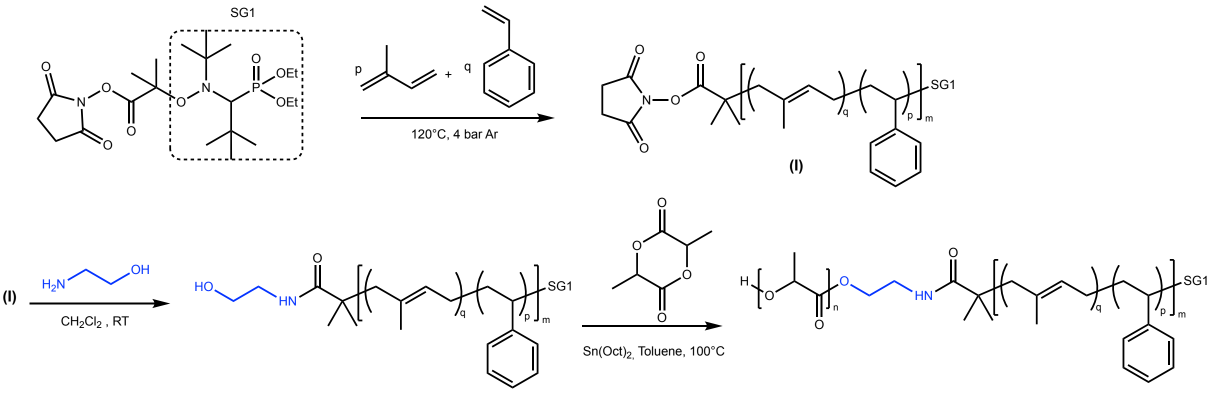


Figure 4*: Synthesis route for preparing PLA-b-PS chains.*

The PEO-containing terpolymers will be synthesized in three steps as presented in **Figure 5**. Mono-hydroxyl-terminated PEO, commercially available at 10 kg mol^{-1} and 20 kg mol^{-1}, will be used as starting block. The alcohol end-group of PEO will be used to perform an intermolecular radical 1,2-addition (after acylation with acryloyl chloride) with the BlocBuilder to obtain the macroalkoxyamine for the polymerization of second and third monomers by NMP.[35]

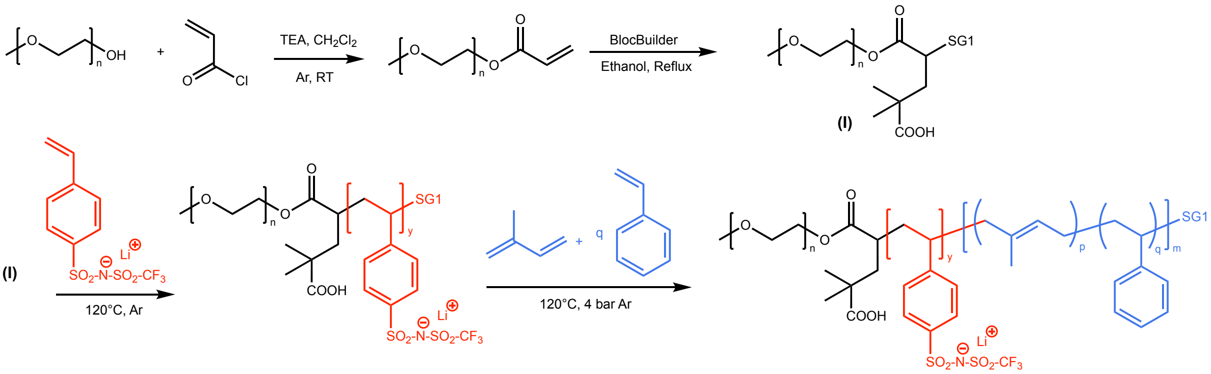


Figure 5*: Synthesis pathway of PEO-based ACB-type block copolymers.*

At each step of reaction, the resulting product will be thoroughly characterized in term of chemical structure, composition and molecular weight by IR, NMR and SEC. As we target the double gyroid and cylindrical phases, the weight fraction of removal blocks will be in the range of 30 and 40 wt%[22] and their average-number molecular weight (M_n) fixed at 10 kg mol^{-1} and 20 kg mol^{-1}. Hence, membrane porosity is expected to be around 25 – 35 % once the degradable block will be fully eliminated. In addition, the elasticity and glass transition temperature (T_g) of the matrix block can be easily tuned by varying the ratio between isoprene and styrene units. In a practical point of view, the targeted T_g will be in the range between 50 – 70°C and will be measured by DSC. This sub-task will deliver several grams of each DBCP.

Risk assessment

There are no risks for this sub-task because the synthesis of DBCPs are already mastered, described and published by partner ICR.[33–35]

- Sub-task 1.2. Fabrication of DBCP membranes having voided nanochannels with physical continuity through the entire film thickness

Objective: Fabrication of freestanding DBCP membranes endowed with voided DG or vertically aligned cylindrical nanochannels derived from the self-assembly of degradable PLA- and PEO-based BCP chains.

High ionic conductivity is the essential prerequisite of a functional electrolytes. Reducing the thickness of electrolyte film reduces its impedance and improves the performance of the resulting batteries. Meanwhile, the mechanical reliability of solid electrolytes is a key aspect related to safety. Thin solid electrolytes must have sufficient strength to resist fracture or Li dendrite penetration over long-term cycling. In a recent review, Wu et al.[36] recommended to reduce the thickness of the solid electrolyte membranes below 25 μm to potentially realize high gravimetric/volumetric densities.

To maximize the σ within DBCP membranes, a nanostructure with perfectly aligned and uninterrupted voided nanochannels from one electrode to another is preferred since vertically aligned ion conducting pathways have a tortuosity equal to unity. However, controlling the nanochannel orientation within several micrometer thick membranes remains challenging. To achieve this main objective, isoporous DBCP membranes endowed with vertically aligned cylindrical domains will be manufactured in ***2POLI*** by using our original methodology combining the non-solvent induced phase separation (NIPS) process with a solvent vapor annealing (SVA) treatment prior to remove the degradable block. Indeed, we have recently demonstrated the formation out-of-plane cylinders having an alignment persistence over 15 μm within solvent-annealed triblock terpolymer films generated by NIPS.[26] Alternatively, an appealing approach to manufacture several micrometer thick NPEs with continuous and uninterrupted voided pathways is to produce a DG morphology with ion conducting nanochannels derived from the DBCP self-assembly. Here, the DG phase, having a moderate tortuosity of ~1.25,[37] can transport ions through all three directions, which will facilitate the evaluation of the Li^+ conduction perpendicular to the membrane (*i.e.*, the ion transport in more relevant through-plane direction). As proof of concept, we have recently manufactured BCP membranes entirely composed of Li^+-conducting DG nanochannels (**Figure 6a-c**). In this study, we showed that the creation of ion conducting DG nanochannels can enhance the ion transportation capacity of SPEs since substantially lower σ were measured from analog films having a nominally disordered as-cast state (**Figure 6d**).

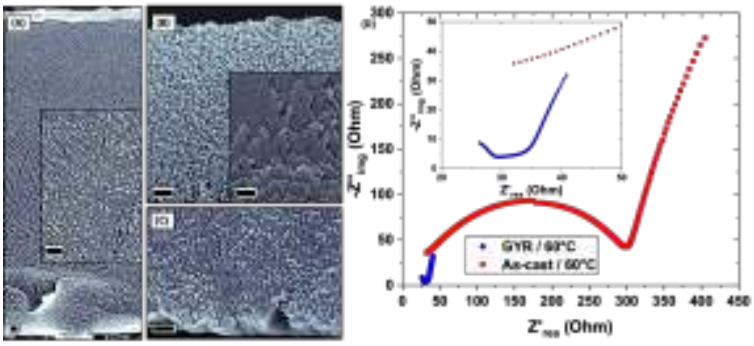


Figure 6: *Cross-sectional SEM views of a 25 µm thick BCP layer generated by NIPS-SVA showing (a) the presence of large gyroid grains within the entire film thickness and details of the DG structure in the vicinity of the (b) top and (c) bottom film regions. Insets (a) and (b) show a stack of gyroid planes and the pattern (i.e., nanochannels arrangement) formed in these planes, respectively. (d) Nyquist plot of SPEs endowed with a (blue) GYR or (red) DIS (as-cast) phase. Data recorded at 60°C clearly evidence that the ion transport is faster for the blue dotted curve exhibiting two partly formed semicircles due to the formation of GBs within the GYR phase (see inset). Scale bars: 500 nm.*

Thanks to the presence of isoprene units in the matrix, if needed, **the mechanical property of nanoporous membranes can be raised by photo-crosslinking of matrix chains**. For this, a phenone-based photo-initiator will be added in the DBCP solution, and the resulting membrane will be exposed to UV-irradiations. To generate voided membranes, the PLA-based DBCP films will be placed in an aqueous alcohol mixture containing sodium hydroxide while PEO-based DBCP layers will be immersed in an aqueous HI solution. The elimination of PLA and PEO blocks from their respective nanostructured membranes will be monitored by either ATR-IR or ^{1}H NMR analysis.

The formation of PLA- and PEO-based nanoporous membranes endowed with voided cylindrical and DG nanochannels will be mainly characterized by AFM, SEM and GISAXS. Additionally, the presence of voided nanochannels within the desired freestanding nanoporous membranes will be attested by measuring variations in water fluxes before and after the removal of PLA- and PEO-based blocks by using a conventional dead-end filtration cell. On the other hand, the real open porosity of nanoporous membranes can be calculated thanks to Archimedes methods by immersing the latter in pure water for a sufficient duration and the porosity (ε) will be calculated by the following equation:

$$\boldsymbol{\varepsilon = (W_1 - W_0)/(\rho \times A \times l)}$$

Where ρ (g cm^{-3}) is the density of pure water, A (cm^2) is the membrane area, and l (cm) is the membrane thickness. W_1 and W_0 are the weight of the membrane before and after saturating in pure water.

Risk assessment

*As we already proved that the NIPS-SVA method is a power tool to generate complex phases (e.g., perforated lamellae, core-shell DG and alternating double diamond structure) as well as square arrays of vertically aligned nanoporous cylinders over 15 µm thick films, we look forward with confidence that NPEs with the desired nanostructure will be achieved in **2POLI**. The main risk could be a lack of significant control on the orientation of the cylindrical nanodomains. As fallback, to better control the orientation of voided domain, we will use the similar blending strategy that allowed us to produce perpendicular P2VP cylinders with an unprecedented alignment persistence.*

*Although vertically aligned nanoporous cylinders are highly desired in **2POLI** and we will do our best to produce them, nevertheless DBCP membranes with non-perfectly aligned nanopores could anyway be used as NPEs by filling them with a liquid electrolyte before studying their properties.*

- Sub-task 1.3. Custom synthesis of lithium salt derivatives and loading of liquid electrolytes into nanoporous membranes

Objective: Synthesis of Li-salt derivatives and their loading within the pores of DBCP membranes.

Three types of liquid electrolyte will be used to fill nanoporous membranes:

1) Solution of lithium bis (trifluoromethanesulfonyl) amide (LiTFSI) at 1 mol L^{-1} in ethylene carbonate will be used as **the reference liquid electrolyte**. One can also replace ethylene carbonate by phosphonate solvents such as triethyl phosphate or cyclic phosphonate solvent, known for their non-flammability.[38]

2) The second liquid electrolyte system that will be considered in ***2POLI*** is a mixture of LiTFSI : [BMIM][TFSI] (1:4 ; mol/mol) where [BMIM][TFSI] is a common imidazolium-based ionic liquid largely studied[39] and BMIM stands for 1-butyl-3-methylimidazolium. Ionic liquids (ILs) are nonflammable, thermally stable molten salts of organic cationic and anionic molecules with negligible vapor pressure. The application of ILs as electrolytes represents an environmentally friendly, durable, and safe alternative to the currently used organic solvents in LIBs.

3) Oligomer of poly(trimethylene carbonate) or poly(ethylene glycol) bearing two TFSI anions will be synthesized and used as liquid electrolyte. TFSI anions are attached to an oligomer structure in the aim to slow down their diffusion and hence, increase the transference number t_{Li^+}. **Figure 7** shows a schematic representation of the third type liquid electrolyte.

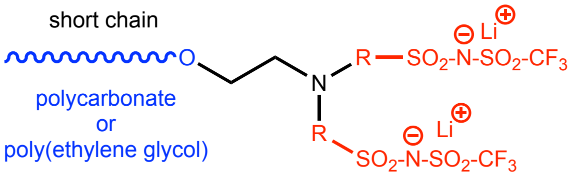


***Figure 7** : Schematic representation of electrolyte structure*

An infiltration methodology will be mainly used to load the various Li electrolytes within the voided nanochannels of polymer membranes. To this end, the functional nanoporous membranes will be infused with the desired lithium salt solution until optimizing the electrolyte loading within isoporous pathways. The liquid electrolyte uptake of membranes will be measured by the weight difference of membranes before and after liquid electrolyte soaking. The dried mass of NPE membranes will be measured with a membrane size of 2 cm × 2 cm. The test process will be carried out in a glove box to prevent water absorption for sufficient duration with continuous recording the mass change of membrane. The liquid electrolyte uptake of membranes will be calculated by the following equation:

$$\mathbf{P = (W-W_0)/W_0 \times 100\%}$$

Where P (%) is the electrolyte uptake of NPE membrane, W_0 (g) is the weight of dry membranes and W (g) is the weight of wet membranes after soaking into liquid electrolyte.

The thermal stability of nanoporous membranes and NPEs will be analyzed by thermogravimetric analysis (TGA).

Risk assessment

The risk of this sub-task is low because almost all liquid electrolytes are commercially available. In addition, the chemistry used for the synthesis of the third liquid electrolyte is already performed and published by partner ICR.[12,40] Infusing liquid electrolyte inside the nanopores of nanoporous membranes does not present *a real risk because the pores walls are hydrophilic and hence will facilitate their infiltration by the envisaged polar liquid electrolytes.*

Task 2 (LLB/LEPMI): Physical characterization and ionic conduction properties of NPEs.

Task leader: Jean-Marc Zanotti
Main participants: R. Bouchet (LEPMI), M. Mermoux (LEPMI), PhD student 1 (ICR-LLB) and PhD student 3 (LEPMI)
Duration: M6 – M42

This task is dedicated to the characterization and mapping the molecular dynamics at nanometric level with the macroscopic behaviour of the materials. Such characterization is accessible through scattering techniques (SAXS and SANS). Using the strong H/D neutron contrast, it will be possible by "Contrast Matching" to characterize the full and uniform filling pores of the matrix by the electrolyte. Also, Neutron Zero Average Contrast will make it possible to characterize the conformation of a single polymer chain under confinement.[27] Ionic transport in NPEs will be characterized in detail by PFG-NMR (to determine and isolate the temporal motion of each charged species as well as the polymer host) and electrochemical impedance spectroscopy (EIS) to study their effective ion conducting properties. The goal of this central task is to select rapidly the best NPEs in term of σ and t_{Li}^{+} for the targeted application by permanent feedback between partners and other tasks. Once the best candidate will be selected, Incoherent Quasi-Elastic Neutron Scattering will be conducted to provide along with the PFG-NMR a time and spatial multiscale view of the confined Li-based electrolyte dynamics from the molecular (ps) to the µm (ms) scales. All these physical characterizations will allow a deep understanding of structure-property relationships of NPEs.

- Sub-task 2.1. Multi-scale dynamic of ionic species in the nanochanels of NPEs

<u>Objective</u>: *Probing the confined electrolytes dynamics from pico to microseconds. For the PEG polymer electrolytes, Zero Average Contrast twill be use to probe the dynamics of a single chain.*

Our group has an on-hand experience of probing the dynamics of electrolytes under nanometric confinement in 1D porous systems. We have used Anodic Aluminum Oxide (AAO, **Figure 8a**) and Vertically Aligned Carbon Nanotubes (VA-CNT, **Figure 8b**). In AAO, the confined material was PEO above the critical entanglement molar mass (Mc = 3600 g mol^{-1}) and the melting temperature (T_m = 60°C). In VA-CNT, two electrolytes have been used: imidazolium ionic liquids (IL) and liquid PEO (500 g/mol) both charged with 1M LiTFSI. As in ***2POLI***, these two systems were envisioned as separator for all solid lithium batteries. In these projects, ICR has grafted short poly-IL chains on the VA-CNT tips to give them an electric insulating character. The ionic conductivity of the confined IL was increased by an order of magnitude compared to its bulk analogue.[41] The ionic conductivity of the PEO electrolyte is equal at room temperature to the classical value of this quantity at 80°C.[42] This advance could be a way to avoid the heating of polymer-based batteries (typically the Blue Solutions technology). Several patents have been filled.[43–45]

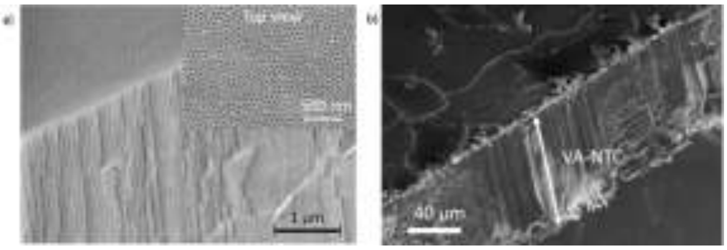


***Figure 8**: a) Scanning Electron Microscope (SEM) image of a typical AAO membrane. The highly oriented array of cylindrical pores (diameter 20 nm, length 100 mm) goes from the top down to the bulk of the membrane. b) Porous VA-CNT composite membrane. The porous moiety is the CNT cores (diameter 4 nm).*

To illustrate the experimental strategy for a multiscale study of the ***2POLI*** electrolytes, we take the case of the AAO confined PEO as an example. This work has been synthetized in a manuscript[46] written for a French-Swedish neutron school. The theoretical development will be found there and spare the reader with these aspects. The multiscale dynamics we propose will rely on the use of a suite of spectrometers all available at the Institute Laue Langevin (ILL, Grenoble, France) where Jean-Marc Zanotti is working permanently (but reports to LLB).

For the short local scale (atomic and few tens of ps), we will use the time-of-flight machine SHARP (French CRG, Responsible: Zanotti). We will use hydrogenated PEO (hPEO). The neutron dynamical susceptibility indicates the number of dynamical modes involved in the system (**Figure 9a**). Based on this information it is possible to delineate a numerical model that can be challenged by the Q dependence of the quasi-elastic signal (**Figure 9.b**). The analysis of the intensities related to each mode can be used to extract a so called Elastic Incoherent Structure Factor (EISF), which is a direct measurement of the geometry of the motion involved. In the case of confined PEO, we have shown that a local "jump over two sites" conformational change (sketch **Figure 9b**) with non-dispersive correlation time is coupled to a translation of the whole polymer chain with a dispersive correlation time. Altogether, those two motions give rise to a helical jump (HJ) motion. Its envelope is represented in green the sketch shown on (sketch **Figure 9c**). The jump distance derived is about 2 Å. This HJ motion extends up to 26 Å. As a summary, we reach the conclusion that in bulk the whole PEO polymer chain is sliding, as a whole, along its own physical contour.

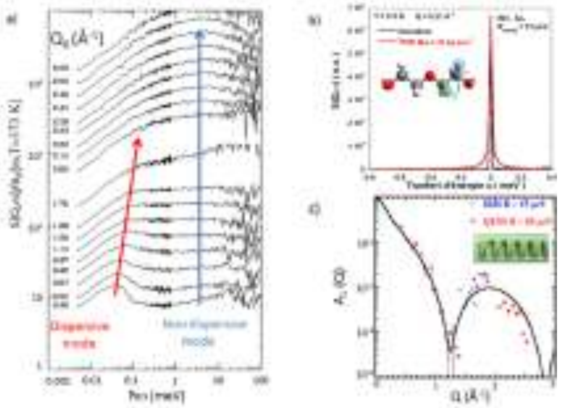


***Figure 9**: a) Q dependent neutron susceptibility of a hPEO melt (100 g mol^{-1}). b) The quasi-elastic signal (in red) stands for the relaxational modes in the system. The instrumental resolution is shown in black. c) EISF of the HJ motion enveloped fitted by the form factor of a powder averaged cylinder of 2 Å in radius and 26 Å in length.*

At the scale of a monomer and at longer time, we will use Neutron Spin Echo Neutron (NSE) on the ILL instrument WASP. The spectrometer can measure correlation times up to few ns. We will then directly access to the Rouse dynamics. By taking the advantage of the macroscopic orientation of pores, we should have access to the radially and longitudinally quantities. In the example presented in **Figure 10**, no striking difference was detected. In ***2POLI***, we expect that the narrower pore diameter of around 10 nm will exalt the anisotropic dynamics. This is in particular true for the polymer-based electrolyte that carries more than 10 monomer units.

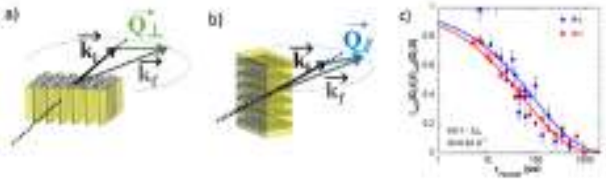


***Figure 10**: The orientation of a macroscopic 1D porous sample in the incident neutron beam (incident $\vec{k}_i$ and scattered $\vec{k}_f$) sample makes it possible to probe (alongside $\vec{Q}$) the dynamics radial (a) and longitudinal (b) to the cylindrical pore. c) Intermediate scattering function at 0.62 Å^{-1} of hPEO melt (35 kg mol^{-1}) perpendicular and radial dynamics.*[46]

By using the NSE spectrometer IN15 (ILL), we will extend our multiscale approach to the scale of the whole polymer chain with a correlation times as large as 1 ms (**Figure 11**). For liquids, this will be used a H/D isotopic mixture able to match the contrast of the empty confining material. For the case of a longer PEO based electrolytes (10 nm), this matching condition will offer to be in the ZAC condition so as the SANS scattering signal will be related to a single polymer chain. Beforehand the IN15 experiments, these matching conditions will be checked by SANS on SAM, the new French CRG operated by LLB at ILL. This matching strategy is the key to erase the intense elastic SANS signal of the porous confining material (**Figure 11**) and be able to access the electrolytes dynamics of 1 μs *i.e.* the relevant time scale for the conductivity properties and meet the PFG-NMR data. It is important to note that in ***2POLI***, the T_g of the confining polymer will be at least of 60°C, so that, at room temperature, at which the inelastic neutron scattering will be conducted, its dynamics will not contribute.

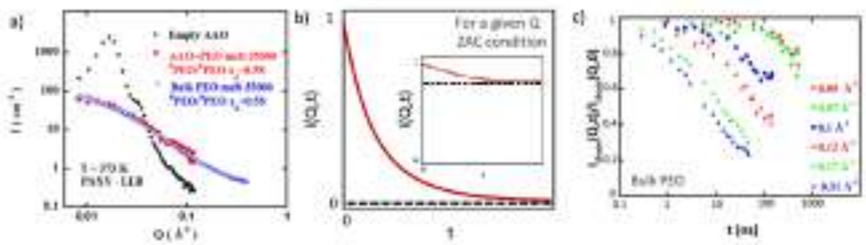


***Figure 11**: a) Under the ZAC condition, the intense SANS spectrum of the empty AAO (black) vanishes and the only scattering contribution is the one of a single polymer chain. These*

matching conditions will also erase(b) the elastic contribution (inset) of the confining material that would prevent the dynamical measurement up to 1 μs.[27]

- Sub-task 2.2. transport properties of NPEs

Objective: Analyzing the ionic charge transport processes as function of functionality and topology of nanochannels (task 1.2) as well as the liquid electrolytes nature.

One of the basic functional properties of an electrolyte is the ionic conductivity. The first aim of this sub-task is thus to quickly screen the transport properties of the NPEs developed in Task 1 to rapidly converge to the best material to feed the Task 3-Electrochemical characterization and battery prototypes. In addition, we need to understand the key parameters that drives the effective conductivity to custom the material chemistry in Task 1. The ionic transport properties of all prepared NPEs will be investigated using both EIS and PFG-NMR. All experimental cells will be assembled in a dry glove box in order to prevent water absorption.

The conductivity will be measured by electrochemical impedance spectroscopy (EIS) on symmetric Stainless steel (SS)/NPEs/SS cells as function of temperature. A comparison with the conductivity of the reference neat liquid electrolyte will help to understand the impact of NPE mesostructuration (tortuosity). The transport anisotropy will be also evaluated by measuring both through-plane and in plane conductivity thanks to a recently developed methodology in the lab.[47] In addition, Li/NPE/Li symmetric cells will be assembled and characterized by EIS to probe at low frequency the diffusion process. In another hand, Bruce and Vincent's method based on chronoamperometric experiments, together with potential relaxation experiments, will enable us to estimate the cationic transference number, t_{Li+}, and the Li^+ diffusion coefficient.[47] These measurements are systematically evaluated as a function of temperature within the range of 10 to 60°C.

From the PFG-NMR experiments, we can measure self-diffusion coefficients of lithium cation and fluorine anion as well as the solvent/polymer dynamic, to assess the transport dynamics in both bulk phase and in confined NPE. From the diffusion coefficients, one can calculate the ionic conductivity (σ_{NMR}) using the Nernst-Einstein equation. However, in NMR measurements, the transport properties of the dissociated and associated Li^+ species in the equilibrium state cannot be distinguished.[48] Thus, the combination of EIS and PFG-NMR measurements allows calculating the Haven ratio, $\sigma_{NMR}/\sigma_{EIS}$, which provides an evaluation of the ion dissociation degree. Indeed, when $\sigma_{NMR}/\sigma_{EIS} = 1$, all ions contribute to conduction on all time scales and are fully decoupled from each other, whereas ratios >1 indicate associations among ions. To correlate the Haven ratio, and the solvation process, confocal Raman spectroscopy will be used to probe the ionic interactions within the electrolytes both in the bulk and confined in the NPEs.

These knowledges are of fundamental importance and can be supported by the multiscale dynamic's properties probed in Task 2.1, to extract the physico-chemical determining parameters that will help in return the optimization of the NPEs.

Risk assessment

Once the NPEs will be achieved in Task 1, their characterization presents only a limited risk.

• Task 3 (LEPMI): Electrochemical characterization of NPEs and battery prototypes.

Task leader: Renaud Bouchet
Main participants : P. Soudant (LEPMI), M. Mermoux (LEPMI) and PhD student 3 (LEPMI)
Duration : M18 – M48

The electrochemical behavior of the best nanoporous polymer electrolyte membranes synthesized in Task 1 and selected from Task 2 will be analyzed in details to further narrow the selection of the most suited electrolyte membranes to be implemented in LMB. Besides transport properties addressed in Task 2, a good electrolyte must also present a wide electrochemical stability, *i.e.* stable interfaces towards the negative and positive electrodes. In addition, the electrolyte must be an efficient barrier to the dendritic growth, and must present a high faradic efficiency versus lithium plating/striping processes, which are the main issues for lithium metal-based technologies. Finally, the ultimate proof of the feasibility and the interest of our new electrolytes will be provided by using the optimized electrolytes in complete Li-metal battery prototype.

- Sub-task 3.1. Electrochemical stability and Lithium/electrolytes interface characterization

Objective: Selection of the best nanoporous electrolyte membranes according to 1) its electrochemical stability, especially at high potential, and 2) its capacity to mitigate the dendrites nucleation and growth.

Electrochemical stability*:* Asymmetric Li/NPEs/stainless steel (or cupper) cells will be assembled in Argon filled glove box and characterized by cyclic voltammetry at slow rate (0,1 mV/s) at 25°C to determine the electrochemical stability window (ESW) of the selected NPEs thanks to Task 2.

Lithium/NPEs interface*:* Symmetric Li/NPEs/Li cells will be used to analyze the stability of the Li/electrolyte interface, and the dendritic growth using both galvanostatic cycling and EIS experiments. Dendrite growth will be characterized at 25°C by cycling the symmetric cells at different current densities spanning (J) from 0.4 to 4 mA/cm^2 with an areal surface capacity cycled of 2 mAh/cm^2. A pressure of 2 or 4 bars will be applied on the pouch cell to check its impact on the cycle life of the lithium electrode. We will analyze *operando*, *i.e.* along the cycling, thanks to EIS the evolution of the interfaces. For a given electrolyte, Li dendrite growth induces either a loss of contact (delamination, electrolyte reduction and consumption, gaseous byproducts, etc), or a short-circuit after a certain number of cycles corresponding to a total amount of coulombs, Q°, that has been exchanged between the two electrodes. This simple procedure enables to discriminate quickly and efficiently the electrolytes by the values of Q° and the impedance allows to understand the origin of the failure.[49,50] After cycling, post-mortem analysis, such as SEM and in-situ X-ray tomography analysis will be carried out to observe the microstructure of the lithium at the interface.[51]

Finally, the faradic efficiency will be analyzed by cycling Li/NPEs/Cu cells with 2 mAh/cm^2 of capacity exchanged at each cycle for 20 cycles. The evolution of delivered capacity and polarization upon cycling will give the information needed to determine the faradic efficiency. Herein, the EIS contribution will also play an important role to understand the behavior of the Cu/NPEs interface as a model of lithium free negative electrode.

- Sub-task 3.2. Assembly and test of scale-lab battery prototype

Objective: Demonstrating the feasibility of lithium metal-based batteries operating at RT with high cyclability and power performances.

For the best NPEs (high σ and t_{Li}^{+}, large electrochemical window stability (EWS) and smooth lithium platting/stripping), lab-scale battery prototypes (10 to 50mAh) will be assembled in pouch cell configuration using model active materials (LMFP, Co&Ni free AM, or SOA NMC811). Composite porous electrodes with a loading of 2 mAh/cm^2 and a porosity around 25% will be elaborated in the LEPMI battery platform. The lithium electrode thickness will be below 50μm. Finally, the obtained batteries will be cycled at 25°C and different C-rates (from $C/5$ to $10C$) to evaluate their performance in terms of cyclability, power and energy density.

Risk assessment

*There is no specific risk in this task. The only limitation will be the quantity of polymer electrolyte available, in fact the experiments in Tasks 3.1 and 3.2 will need electrolyte batches of several grams. However, **ICR** and **IEM** partners are confident about providing such required quantities for the best-identified materials thank to their strong expertise in polymer synthesis and nanoporous membranes fabrication respectively.*

Task schedule, milestones and deliverables

Gantt diagram

Tasks	Year 1				Year 2				Year 3				Year 4			
	3	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48
Task 1 : ICR & IEM	**Elaboration of nanoporous polymer electrolytes**	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦						
1.1- Degradable BCPs	🟦	🟦	🟦	🟦												
1.2- Nanoporous membranes		🟦	🟦	🟦	🟦	🟦	🟦									
1.3- NPEs		🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦						
Task 2 : IEM, LLB, LEPMI			**Multi-scale characterizations**	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧				
2.1- Ions Dynamics			🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧					
2.2- Ions Transport				🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧				
Task 3 : LEPMI						**Lithium metal lab battery prototype**	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
3.1- Electrochemical						🟩	🟩	🟩	🟩	🟩	🟩	🟩				
3.2- Battery Prototype										🟩	🟩	🟩	🟩	🟩	🟩	🟩
Non-permanent staffs																
PhD 1 (T 1.1, 1.3, 2.1)	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				
PhD 2 (T 1.2, 1.3)			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		
PhD 3 (T 2.2, 3.1, 3.2)				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
Scientific & financial reports				R1				R2				R3				R final

Deliverable and milestone description

Task 1 D1.1 (M1 – M6): Synthesis and characterization of different DBCPs
D1.2 (M3 – M24): Fabrication and characterization of nanoporous membranes
D1.3 (M6 – M30): Synthesis and characterization of customized liquid electrolytes and preparation of NPEs

M1 : Nanoporous polymer electrolyte membranes

Task 2 D2.1 (M6 – M36): Overall characterization of the multi-scale structure and dynamics functions in NPEs
D2.3 (M9 – M36): Characterization of ionic transport properties (σ, D_{Li+}, t^+, degree of dissociation, tortuosity)

M2 : Structure-Dynamic-Ionic transport properties relationships

Task 3 D3.1 (M18 – M36): Determination of the electrochemical stability window
D3.2 (M24 – M36): Characterization of the Li/electrolyte interface behavior in open circuit potential and under current along with dendrite growth on selected electrolytes
D3.3 (M30 – M48): Li metal polymer battery assembly and cycling.

M3: Lithium metal lab battery prototype

d. Ability of the project to address the research issues covered by the chosen research theme

2POLI project aims at the development of innovative nanoporous polymer electrolytes for safe LMBs, which is at the heart of the field "Transition énergétique" and in line with BATTERY 2030+ program launched by European Union, thus ***2POLI*** is relevant to CES 05/axe H9 « Une énergie durable, propre, sûre et efficace». The ***2POLI*** project is interdisciplinary; it will gather expertise in chemistry, physical chemistry, physics, materials science and electrochemistry. Thus, the best funding source is a PRC "Projet de Recherche Collaboratif".

II. Organisation and implementation of the project

The success of the 2POLI project also requires a strong coordination due to its interdisciplinary. Dr. Trang Phan of ICR lab will be the coordinator of the ***2POLI*** project and will take the responsibility for ensuring that the work planning is kept to its schedule and that milestones are reached upon completion of the project objectives.

The management task will consist in ensuring that exchanges between all people involved are effective for an overall progress in the objectives of the project. This includes maintaining direct contact between partners, leading the coordination between tasks and the production of deliverables and milestones in due time always in respect of the objectives and determining the dissemination of results (patents, publications in scientific journals, congress participations). Especially, after taking industrial properties, the results will be used to approach the industrials of the sector (Solvay, Arkema, SAFT, Blue Solutions, ...). In addition, as the four tasks proposed are linked, it is thus crucial that each partner knows, in real time, the questions to be solved and the benefits from the input of the others. Each task is thus coordinated by a task leader. They will control the progress of the scheduled work within the tasks in terms of technical achievement and planned deliverables tasks and will report the on-going task progress to the coordinator (Dr. Trang Phan) in a written document every three months. Regular meetings between partners will take place every six months, plus whenever the coordinator, or a partner feels it is necessary. This will be completed by exchanges through informal e-mails and phone discussions. Review and evaluation of milestones and definition of strategies for the next steps will be discussed among consortium members.

a. Scientific coordinator and its consortium

Coordinator: Dr. **Trang Phan** (Associate Professor), from the Institut de Chimie Radicalaire - Marseille, will lead ***2POLI*** project. She has been previously coordinator of one ANR grant (SELPHy) and involved in several ANR grants both as scientific leader and partner. She has solid skills in the macromolecular engineering, synthesis and characterization of porous polymers and nanostructured materials and is co-author of 11 patents and 79 publications. She will devote 37,5% of her time for the design and preparation of DBCP as well as the coordination of ***2POLI***.

Consortium: ***2POLI*** will gather four teams of expert in *i)* macromolecular design and synthesis, *ii)* BCPs self-assembly, *iii)* characterization of dynamic (macro)molecular and *iv)* ionic charge transport in materials.

Partner 1 – ICR: The team from ICR including Dr. Marion Rollet and Dr. Didier Gigmes, recognized for its expertise in the synthesis of hybrid materials and complex macromolecular architecture.[40] This team and PhD-1 will carry the synthesis and characterizations of the structure and composition of degradable block copolymers and Li-based electrolytes.

Partner 2 – IEM: Dr. **Karim Aissou** is a CNRS researcher with strong expertise on the self-assembly of BCPs of interest in various high-tech applications while Arie van der Lee is a CNRS Research Engineer with expertise on SAXS and GISAXS techniques. This team together with PhD-2 and M.Sc. student will carry the manufacturing of nanoporous electrolytes membranes and their characterizations.

Partner 3 – LLB: The scientific expertise of Dr. **Jean-Marc Zanotti** (JMZ) in the field of confinement is recognized at the international level. JMZ has received the Schlumberger price of the French Academy of Sciences for results on confined water. JMZ has a strong experience in SANS and QENS and published several papers on multiscale studies under 1D confinement, specially IL[52] and PEO[46] conduction under 1D confinement. JMN and PhD-1 will perform all X-ray and neutron scattering experiments.

Partner 4 – LEPMI: Renaud Bouchet, Professor at the National Polytechnic Institute of Grenoble (G-INP) and Director of the Lithium and interface joint lab between LEPMI and Blue Solutions, is an expert of ionic charge transport in organic materials (liquid, gel, polymer, or composite) and of the electrochemical characterization especially in the context of lithium metal-based batteries. Dr M. Mermoux will conduct Raman spectroscopy experiments. P. Soudant will perform PFG-NMR experiments to measure the lithium diffusion coefficient in different porous membranes. Together with the recruited PhD-3, this team will study electrochemical properties of porous membranes and their application in lab-scale LMBs.

Implication of the scientific coordinator and partner's scientific leader in on-going projects

Name of the researcher	Person. month	Call, funding agency, grant allocated	Project's title	Name of the scientific coordinator	Start - End
Trang PHAN	12	PRCE/ANR/529 k€	ARES, Alkoxyamines as safe surrogates to peroxy and azo compounds	MARQUE	2020–2024
	9	PRC/ANR/420 k€	ELECTRON, Enhanced structural understanding of functional polymers by solid-state DNP NMR	ZIARELLI	2020–2024
	12	PIA4/BPIfrance/23.1 M€	ELIAS, Éléments lithium avancés tout solide	TRAN (SAFT)	2023 - 2026
	9	Int. Res. & Training /A*Midex/720 k€	ION-MEET, Ion conducting materials for electrochemical energy technologies	PASQUINI	2023 - 2026
Karim AISSOU	4	PRC/ANR/561 k€	SESAME, Shear oriented ionic self-assemblies for optimized ion transport	MANDIL-JAKANI	2023 - 2026
	8	PRC/ANR/605 k€	ACECANISME, Acylated acetals: a chemical platform for advanced covalent adaptable networks and isoporous functional membrane	LADMIRAL	2023 - 2026
Jean-Marc ZANOTTI	3	PTC, CEA, 120 k€	YESWECAN, ARN sequencing by CNT confinement	ZANOTTI	2024-2026
	1	PEPR H2, 4.3 M€	PEFMC95, Piles à combustible à membrane échangeuse de protons à 95°C.	CHATENET	2023-2025
	1	ERANET, 448 k€	NAMEAS, Anisotropic membranes for fuel cells	GURSEL	2024-2027
Renaud BOUCHET	8	PRCE/ANR/452 k€	TATABATT, Single-ion polymer electrolyte for LMB	DROCKENMULER	2022-2026
	6	MSCA DN 2022/2.7 M€	RIDERS, Ionic transport in polymer and gel electrolyte	DROCKENMULER	2023-2027
	15	Labo commun/8 M€	Li2, Lithium metal and interfaces	BOUCHET	2022-2027

b. Implemented and requested resources to reach the objectives

Partner 1: ICR

Staff expenses (120 k€)

The ***2POLI*** project is a multidisciplinary project that is an excellent environment for training young scientist. Hence, a PhD fellowship (36 months) will open at ICR and share with LLB. The Ph.D. student will contribute to the preparation of block copolymers and the macromolecular characterizations (Sub-tasks 1.1 and 1.3) as well as the physical characterizations using scattering techniques (Sub-task 2.1). This work requires a student with a good background both chemistry and physic of polymers. The Ph.D. student will be supervised by Dr Phan and Zanotti and the cost for 36 months is estimated at 120000€.

Instruments and material costs (25 k€)

The requested funding of this section is mainly for synthesis experiments and materials purification and characterization. We estimate our needs to 15000 € for chemicals (reagents, catalyst, anhydrous solvents, deuterated solvents) and 6000 € for small laboratory equipments such as stirring and heating plates,

vacuum equipment, mechanical stirrer, electronic devices for temperature control and reaction monitoring, glassware, ….
The success of this project relies on the use of several instruments – DSC, ATR-IR, chromatography machines – which require maintenance with a cost at 4000 €.

Outsourcing / subcontracting (7 k€)

Additional costs have to be considered for some particular analyses at technical platform of Aix-Marseille Univ., namely elemental analyses, ^{1}H, ^{19}F and ^{13}C NMR measurements (5000 €). Cost for chemical wastes treatment is estimated at 2000 €.

Overheads costs (30.05 k€)

Mission fees to assist to semester meetings organized by the other partners are estimated at 2000€. A participation of 5000€ (for the PhD student and 2 permanents) to attend national congress and international congress is requested.
For administrative managing and university fees are at 14.5% affording a cost of 23 055 €.

Partner 2: IEM

Staff expenses (131 k€): A Ph.D. student (36 months, starting at t0 + 3 months, 125706 k€) will be recruited to study the self-assembly of DBCP chains into NPEs that will subsequently infiltrate with the desired Li- based electrolyte (**Sub-tasks 1.2 and 1.3**). The Ph.D. student will carry out the optimization of the SVA processes for the stabilization of the vertically-aligned cylindrical phase as well as the DG nanostructure in close collaboration with a M.Sc. student (6 months, 5 k€) that will complement the task force at IEM.

Instruments and material costs (25 k€): 10 k€ will be dedicated (*i*) to update the SVA set-up that will be used to promote the self-assembly of BCP chains, (*ii*) to partially renew the home-made plasma etch tool that will be used selectively etch the desired block in order to improve the AFM and SEM contrasts. To ensure the smooth running of the project, an amount of 15 k€ is also requested to cover costs associated to the membrane fabrication (solvents, gas, substrates) as well as the structural (AFM tips) characterizations.

Outsourcing / subcontracting (2 k€): An additional 2 k€ is included for publication and intellectual property costs.

Overheads costs (3 k€): Scientific outputs will be presented in conferences and scientific visits among partners (permanent staff and Ph.D. student) will be organized.
The administrative managing and university fees are at 14.5% affording a cost of 23 302 €.

Partner 3: LLB

Instruments and material costs: 5 k€ will be devoted to the purchase of an electrochemical cell for *in-situ* conductivity measurements during dynamic experiments (See PhD Pinchart)[42]. Associate to this equipment, 10 k€/year of disposable and small equipment will be necessary for the 3 first years and 5 k€ for the last year.

Overheads costs (7k€). Scientific outputs will be presented in conferences, on the WEB sites and communication supports of CEA and scientific visits among partners (permanent staff and Ph.D. student) will be organized. The administrative managing and CEA fees are at 14.5% affording a cost of 6815 €.

Partner 4: LEPMI

Staff expenses (120k€)

36 months of PhD are necessary to perform the proposed tasks. The candidate should have a solid formation in electrochemistry, as well as a good knowledge in physico-chemical characterization of materials, and ideally an experience in batteries. He/she will participate to the ionic transport characterizations of the NPEs (subTask 2.2) and the study of their electrochemical properties in LMB (tasks 3).

Instruments and material costs (30k€)

Most of the facilities involved in the electrochemical characterization of NPEs are already available through the LEPMI battery platform (https://lepmi.grenoble-inp.fr/fr/ressources/plateforme-tests-batteries).

However, due to the large number of cells that will be characterized 15 k€ will be used to purchase three dedicated channels (pot/galv + EIS). 15 k€ are requested to purchase the consumables including conductivity cells, coffee bag for pouch cells, copper and aluminum foil, pressure setups for pouch cells, crucibles for DSC and ATG, small laboratory equipment, etc, as well as the glove box management (gazes, gloves, sensors calibration), and the Raman spectroscope annual maintenance.

Outsourcing / subcontracting (6k€)

Those include expenses for characterization techniques that require the use of the technical platforms CMTC from Grenoble INP (i.e. SEM, micro-tomography X, 4 k€). These credits will also cover the publication fees (fees for cover, color images, or open access articles, 2 k€).

Overheads costs (31,8k€)

Those include mobility expenses covering collaborative experiments; periodic meetings; research and training mobility of the PhD; promoting our results in the best (inter)national conferences (8 k€).
They also include a flat rate corresponding to 14,5% of eligible direct costs (23.8 k€).

Requested means by item of expenditure and by partner

	Partner 1 *ICR*	**Partner 2** *IEM*	**Partner 3** *LLB*	**Partner 4** *LEPMI*
Staff expenses, including costs of a partial release from teaching obligations in a JCJC project	120 000 €	131 706 €	0 €	120 000 €
Instruments and material costs	25 000 €	25 000 €	40 000 €	30 000 €
Building and ground costs	0 €	0 €	0 €	0 €
Outsourcing / subcontracting	7 000 €	2000 €	0 €	6000 €
Overheads costs	7 000 €	3 000 €	7 000 €	8 000 €
Administrative management & structure costs	23 055 €	23 302.37 €	6 815 €	23 780 €
Sub-total	**182 055 €**	**184 008.37 €**	**53 815 €**	**187 780 €**
Requested funding	**607 658 €**			

III. Impact and benefits of the project

The development of this research project is expected to yield a breakthrough that would permit to respond to the main challenges of **high performance and safe LMBs**. The success of SSLMBs opens new avenues for more sustainable development of energy activities. Indeed, such technology could further broaden to other all- battery technologies such as Li/Sulfur, Li/air or those based on sodium cations. The proposed synthetic approach could be easily extended to complementary anionic exchange membranes for applications such as redox flow battery, sensors, chromatography, etc. On the long term, the results obtained within the project will consolidate the recognition of the involved academic and tighten their collaborations in the process to merge into broader consortiums in view of answering to European calls for project within e.g. Horizon Europe. Potential market is immense and this project could lead to the creation of Gigafactories throughout Europe and abroad. This battery technology could also be integrated in other applications where security and energy density are key, such as for energy storage, military applications or other mobility markets.

The whole group has a successful past in valorization of fundamental and applied research via patents and publications. Valorization also includes communications in national and international conferences. The development of this project should have a strong scientific impact at different levels in terms of valorization. In the field of result protection and exploitation, all partners have a strong history in applying patents. As such, any systems of interest will be patented by the teams involved in this aspect of the research. In addition to the potential patents, this innovative research project will permit to continue and expand the publication of significant results in scientific journals with high impact factors as we are used to do for several years (e.g. *Nat. Mater., Nat. Energy., Angew. Chem Int. Ed.*, *ACS Macro Lett.*, *Macromolecules*, *Chem. Commun*.). As the group consists of members who are regularly invited to conferences, it is expected that the work emanating from this project will be equally presented at such level. Furthermore, each partner will participate to International Conferences in his expertise field. As the project is interdisciplinary, a large part of the scientific community will be concerned.

Concerning the setting up of actions towards teaching at university, the group is composed of Professors and Assistant Professors teaching at engineering school and master level in their specialties (polymers, electrochemistry, materials characterizations). The scientific approach developed in this project will be presented during these lectures.

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