



# Influence of different salts in poly(vinylidene fluoride-co-trifluoroethylene) electrolyte separator membranes for battery applications



C.M. Costa<sup>a</sup>, R. Leones<sup>b</sup>, M.M. Silva<sup>b</sup>, S. Lanceros-Mendez<sup>a,\*</sup>

<sup>a</sup> Centro/Departamento de Física, Universidade do Minho, 4710-057 Braga, Portugal

<sup>b</sup> Centro/Departamento de Química, Universidade do Minho, 4710-057 Braga, Portugal

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## ABSTRACT

Poly(vinylidene fluoride-co-trifluoroethylene), P(VDF-TrFE) solid polymer electrolytes were prepared using porous membrane soaked in lithium tetrafluoroborate (LiBF<sub>4</sub>), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), magnesium triflate (Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>) and sodium triflate (Na(CF<sub>3</sub>SO<sub>3</sub>)) electrolyte solution.

The effect of the uptake of different salts in the morphology, polymer phase, thermal and mechanical properties of the membrane was determined.

The electrolyte uptake ranged from 396% for the LiTFSI salt to 529% for the Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>. It is observed that ionic conductivity of the membrane is dependent of the anion size of the salts present in the electrolyte solution. Independently of the electrolyte solution, high ionic conductivity is obtained. In particular, the ionic conductivity for the LiTFSI salt increases from 0.32 to 1.2 mS/cm when the temperature is increased from room temperature to 100 °C.

The porous membranes immersed in different electrolyte solutions show good electrochemical stability as determined by cycle voltammetry. It is observed that anion size is very important parameter that affects the uptake value and electric properties of the polymer electrolyte. It is concluded that the polymer electrolyte based on P(VDF-TrFE) porous membranes are adequate for battery separator applications.

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## 1. Introduction

Lithium ion batteries show high energy density (>400 W h kg<sup>-1</sup>) and have been widely implemented in devices such as computers and mobile phones as well as in electric vehicles. There is a strong need to increase the autonomy of batteries through novel material and integration strategies taking into account cost, energy and power density, manufacture simplicity and safety [1–3].

The main characteristics of a lithium-ion battery are being light, cheap, to show a large number of charge–discharge cycles, no memory effect, and environmental friendliness, among others [4,5].

One of the key elements in battery systems is the separator membrane that separates the anode and cathode. The separator membrane is responsible for controlling the number and mobility of the ions and to maintain the liquid electrolyte between both

electrodes [6,7]. It is important to tailor its most important properties such as porosity, electrical and mechanical properties in order to improve battery performance [8].

Many polymers are being used in battery separator such as poly(ethylene) (PE) [9,10], poly(propylene) (PP) [11], poly(ethylene oxide) (PEO) [12,13], poly(acrylonitrile) (PAN) [14,15], poly(methyl methacrylate) (PMMA) [16,17] and poly(vinylidene fluoride) (PVDF) and its copolymers [18–20].

Typically, micro and macroporous polymer membranes swelled in a liquid electrolyte solution with the salts dissolved in an organic solvent are used as separators in lithium ion batteries [21].

The main characteristics of an ideal solvent are its fluidity and high dielectric constant [22]. The high fluidity (low viscosity) of the solvent is important for improving ion transport and the high dielectric constant is relevant for dissolving the salts present in the liquid electrolyte solution [22].

The most used solvents in electrolyte solutions belong to organic esters and ether classes and are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) [21].

\* Corresponding author. Tel.: +351 253 604 320; fax: +351 253 604 061.

E-mail address: [lanceros@fisica.uminho.pt](mailto:lanceros@fisica.uminho.pt) (S. Lanceros-Mendez).

These solvents have different melting temperature, viscosity and dielectric constant and can introduce modifications in the separator that affect the battery performance [23].

Propylene carbonate (PC) has high donor number (DN = 15.1) and acceptor number (AN = 18.3) [24], donor number being relevant for controlling ion-solvating ability of polymer [25]. These numbers deliver information about the interaction of the solvent, a higher DN value leading to a higher performance for the dissociation of the salt.

In general, salts with a polarizing cation and a large anion with a well-delocalized charge, and therefore also with low lattice energy, are the most suitable for their use in polymer electrolytes (PEs) [26,27]. In spite of the dangers associated with the anion, lithium perchlorate (LiClO<sub>4</sub>) is a salt that satisfies the conditions mentioned above. Lithium trifluoromethanesulfonate (or triflate) (LiCF<sub>3</sub>SO<sub>3</sub>) and LiBF<sub>4</sub> have also been extensively employed in this area [28]. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is particularly interesting as a guest species in solid PEs and also one of the best choices. In common with other salts that contain large polarizable anions, LiTFSI has low lattice energy and a low tendency to form ion-pairs, leading to enhanced ionic mobility.

An important factor that determines the properties of the salts is the size of anions. Different anions are studied in separator membranes for lithium ion battery applications, being the most important ClO<sub>4</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)N<sup>-</sup>, BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> [29]. In particular, the (CF<sub>3</sub>SO<sub>2</sub>)N<sup>-</sup> (TFSI<sup>-</sup>) anion shows high thermal and electrochemical stability, moderate price and is non-toxic.

Salt solubility of different electrolyte solution in PVDF membranes was studied by Shiao et al. [30], obtaining high ionic conductivity (>1 S cm<sup>-1</sup>) for electrolyte solution with LiAsF<sub>6</sub> and LiPF<sub>6</sub> salts [30].

Zhang et al. [31,32] have demonstrated that LiBF<sub>4</sub>-based electrolytes are a good alternative to lithium hexafluorophosphate (LiPF<sub>6</sub>)-based materials as components in low temperature Li-ion batteries with improved performance.

The importance of the donor number in the solvating ability of the different polymers was studied, the free-ion fraction being higher when gel-forming matrixes were used. The cation transference number showed the opposite trend, presumably due to the retardation effect exerted by stronger Li<sup>+</sup> polymer interactions [25]. Commonly, the ionic mobility increases through the rapid segmental motions of the polymeric chains for both cations and anions by expanding local free volume [26].

Advances in separator membranes are thus still needed to meet the challenges imposed by the electrolyte solution.

Due to the promising results obtained with P(VDF-TrFE) for battery applications in relation to its high ionic conductivity, good mechanical and thermal properties in comparison to the commercial PE separators [18], the objective of this work consist on the preparation of P(VDF-TrFE) porous separator with salts based in different anions and cations. The salts are constituted by different cations, Li<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> and anions BF<sub>4</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)N<sup>-</sup> and (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>. The performance of the different anions, cations and polymer segments are evaluated and investigated through electrochemical techniques including impedance electrochemical spectroscopy and cycle voltammetry. The morphological, thermal and mechanical properties of the membrane as well as their variations at the molecular level were evaluated together with their electrical properties as a function of the different salts, with the aim of evaluating the suitability of P(VDF-TrFE) porous membranes for lithium, magnesium and sodium-ion batteries. The battery separator with salts constituted by Na<sup>+</sup> and Mg<sup>2+</sup> are more interesting than the ones based on Li<sup>+</sup> as Na<sup>+</sup> and Mg<sup>2+</sup> are cheaper and more available (through natural resources) than of Li<sup>+</sup>. Sodium and magnesium metals also show higher melting temperature [33]. Since sodium is the fourth most abundant element in the earth crust and has

low cost, it becomes an interesting material in the field of energy storage [34].

## 2. Experimental details

### 2.1. Materials

Poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE), 70/30,  $M_w = 350,000 \text{ g mol}^{-1}$ ) was supplied by Solvay. N,N-dimethylformamide (DMF) and propylene carbonate (PC) were acquired from Merck and Sigma-Aldrich, respectively. Lithium tetrafluoroborate (LiBF<sub>4</sub>), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), magnesium trifluoromethanesulfonate (Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>) and sodium trifluoromethanesulfonate (Na(CF<sub>3</sub>SO<sub>3</sub>)) were purchased from Sigma Aldrich. Table 1 illustrates the chemical structure and the molecular weight of the different salts.

### 2.2. Preparation of the polymer separator membrane

The P(VDF-TrFE) membranes were prepared by dissolving the polymer material in N,N-dimethylformamide (DMF, from Merck) at a 15/85 polymer/solvent weight ratio following the procedure described in Ref. [18].

Briefly, the copolymer was dissolved in DMF at room temperature under magnetic stirring until a homogeneous and transparent solution was obtained. In order to prevent the formation of aggregates and to help the dissolution of the powders, the solution was then hold 5 °C above room temperature for 15 min. The solution was then kept within a glass Petri dish in a gas extraction chamber for 15 days at room temperature to complete DMF evaporation.

### 2.3. Electrolyte solution

The membranes were immersed in the liquid electrolyte, consisting of a 1 M solution of LiBF<sub>4</sub>, LiTFSI, Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and Na(CF<sub>3</sub>SO<sub>3</sub>) in PC for 24 h and the uptake was evaluated by Eq. (1):

$$\varepsilon = \left( \frac{M - M_0}{M_0} \right) \times 100 \quad (1)$$

where  $\varepsilon$  is the uptake of the electrolyte solution,  $M_0$  is the mass of the membrane and  $M$  is the mass of the membrane after immersion in the electrolyte solution. P(VDF-TrFE) with of different electrolyte solution will be called hereafter by the salt name: LiBF<sub>4</sub>, LiTFSI, Mg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and Na(CF<sub>3</sub>SO<sub>3</sub>).

**Table 1**  
Chemical structure and molecular weight of the different salts.

Salts	Structure	Molecular weight (g/mol)
LiBF <sub>4</sub>		94
LiTFSI		287
Mg(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>		322
Na(CF <sub>3</sub> SO <sub>3</sub> )		172

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