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# Synthesis and fuel cell performance of phosphonated hybrid membranes for PEMFC applications

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## ABSTRACT

The present work reports on the synthesis of novel organic–inorganic hybrid composites for proton exchange membranes. These original membranes are based on anionically synthesized phosphonic acid polymers, grafted to functionalized silica nanoparticles, and then dispersed in a matrix of poly(vinylidene fluoride-co-hexafluoropropylene), noted poly(VDF-co-HFP). In a first step, poly(vinylphosphonic acid) with different molecular weights (3.2 and 40 kg/mol) were synthesized from commercially available diethylvinylphosphonate and then grafted onto silica. In a second step, various amounts of phosphonic grafted silica nanoparticles, noted SiO<sub>2</sub>-g-PVPA, were dispersed in the poly(VDF-co-HFP) matrix to prepare membranes by solvent casting. Membranes with phosphonated silica particle loadings from 20 to 63 wt% exhibited proton conductivities from 23 to 54 mS/cm in immersed conditions at 80 °C. The highest values were obtained for the membrane with the highest silica content. Interestingly, the corresponding composite membrane, with a loading of 63 wt%, displayed a power density of 800 mW/cm<sup>2</sup> (60 °C, 1.5 A/cm<sup>2</sup>) in single fuel cell tests.

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## 1. Introduction

New alternative conversion technologies are of primary importance today, as various applications are dependent on fossil fuels. Since the directive tends to reduce power source emissions, the fuel cell technology has been considered an attractive energy source as a result of it offering a high energy conversion efficiency, a high power density and low greenhouse gas emissions [1,2].

The industrial scale development of proton exchange membrane fuel cells (PEMFCs) faces the improvement of the intrinsic performance of the fuel cell core, which particularly concerns the polymer electrolyte membrane (PEM). This element is a key component of the PEMFCs, acting as a solid electrolyte proton conductor as well as a separator to gas permeation from the anode to the cathode. The membrane must exhibit good thermal, chemical and mechanical stabilities, low gas permeability, high proton conductivity and finally a long life span [3]. In this context, polyperfluorosulfonic acids (Nafion<sup>®</sup>, Aquivion<sup>®</sup>, Aciplex<sup>®</sup>, Flemion<sup>®</sup>, 3Mlonomer<sup>®</sup>, Hyflon<sup>®</sup>) have been widely studied and have become references as PEM materials thanks to their excellent properties [4].

However, these membranes present high production costs as well as limited performances at operating temperatures above 100 °C, leading to a drastic decrease of the proton conductivity.

Indeed, a sulfonic membrane requires hydration to an extent that is directly connected to the total number of water molecules per sulfonate group (denoted  $\lambda$ ), limiting the operation temperature to below 80 °C [5]. Under such conditions, serious problems appear such as carbon monoxide poisoning of the catalyst layer, a decrease of the cathode kinetics and the gas transport to the electrode, complicated heat and water management and finally lower stability and durability due to the excess of liquid water [6]. To this end, the U.S. Department of Energy has established a guideline [7] of 120 °C and 20% RH as target operation conditions, for a desired conductivity higher than 0.1 S/cm.

During the past decade, significant research efforts have been aimed at developing new alternative membrane materials with enhanced properties and lower cost, able to operate under low humidity and temperatures above 100 °C [8]. With this in mind, several non-fluorinated and fluorinated polymer electrolytes have been developed including sulfonic polysulfone, sulfonic poly(phenylene oxide), sulfonic poly(ether ether ketone), sulfonic poly(aryl ether ketone), perfluorophosphonic acids [9–14], and more recently, terpolymers based on vinylidene fluoride (VDF) and hexafluoropropylene (HFP), grafted by aryl sulfonic acids [15].

In order to reach higher proton conductivities at elevated temperatures, phosphoric acid-doped polybenzimidazole (PBI/H<sub>3</sub>PO<sub>4</sub>) blends have been developed (0.03 S/cm at 150 °C). However, these systems present serious issues of stability over time [16]. To avoid these drawbacks, heterocyclic molecules (imidazole, benzimidazole, pyrazole) have been anchored to polymeric systems via spacers [8,17].

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Heterocycles present the great advantage of a high boiling point allowing operation under drastic conditions. This way, phosphonic acids are protogenic groups which are considered as almost-anhydrous proton-conducting moieties due to the high degree of proton self-dissociation arising from their intrinsic amphoteric character and their high dielectric constant. These entities exhibit fast hydrogen bond cleavage and formation allowing the proton transport via anhydrous conduction mechanism, known as the Grotthuss mechanism [18,19]. It has also been proposed that the conductivity of the phosphonate under nearly zero humidity may mainly be due to the presence of small amounts of water during the self-condensation reaction between phosphonic acid groups [20]. Considering this result, sulfonic acid groups, phosphonic acids groups and imidazole groups have been compared at low humidity (RH < 40%) and temperatures between 120 and 160 °C by Schuster et al. [21]. The authors concluded that phosphonic acids groups were the most suitable proton conductors under such conditions and suggested that they were interesting as protogenic groups for conducting polyelectrolytes. The proton can be transported through an anhydrous conduction mechanism under low humidity conditions or through the dynamics of water, at elevated water contents.

Different types of phosphonated membranes have been developed during the last few years. However, phosphonated monomer polymerization is not easy to set up as very few monomers are commercially available and often have to be prepared [22]. Moreover the polymerization is sometimes difficult, leading to low molecular weight products. One efficient way is to perform polymerization and/or copolymerization of diethylvinylphosphonate (DEVP) monomer via an anionic polymerization process described by Jannasch et al. [23–25]. These living polymerizations are very attractive since they render it possible to easily obtain size-controlled and high molecular weight polymers. Thus, interesting properties could be obtained in such regular materials.

These membranes exhibit a good proton conductivity at high levels of hydration but the conductivity quickly shuts down as water content is decreasing. In order to enhance the water retention, some authors have proposed to introduce silica nanoparticles in poly(vinylphosphonic acid) (PVPA) from 5 to 20 wt% [26]. The best conductivity was obtained with a loading of 10 wt% (0.08 S/cm at 100 °C and 50% HR) but mechanical properties were too poor to prepare thin membranes. Consequently, their relevance for PEMFC applications was limited.

Another way to prepare hybrid membrane is to use the sol-gel process from epoxyhexylethyltrimethoxysilane (EHTMS) as a silica precursor and amino trimethylene phosphonic acid (ATMP) as a phosphonic precursor [27]. The prepared membranes exhibited a relatively high proton conductivity value at 140 °C under anhydrous conditions (45.5 mS/cm). Nevertheless, the conductivity at 20 °C was low (0.088 mS/cm) and no fuel cell test has been reported. This can be due to a reduced performance of the membrane during starting conditions and a low mechanical strength. Moreover, sol-gel processes are usually expensive and sometimes not easy to set up.

Organic-inorganic hybrid composites based on an inert polymer matrix and loaded with inorganic nanoparticles have attracted considerable attention. The organic phase provides the mechanical stability whereas the inorganic one manages the proton conduction as well as the water retention. As in the case of Nafion<sup>®</sup>, hydrophobic and hydrophilic nanophases are present and provide a better performance of the membrane [28]. Indeed, the main-chain-type acid functionalized polymers often display lower proton conductivity compared to side-chain-type acid functionalized polymers because of the less distinct separation between hydrophilic and hydrophobic domains [29]. In the present approach, the non-conducting copolymer involved is the poly(vinylidene fluoride-co-hexafluoropropene) noted poly(VDF-co-HFP) because of its physical and electrical

properties, its low permeability to gases and finally its low cost which make it highly beneficial for fuel cell applications [30]. On the other hand, the inorganic phase is incorporated using functionalized fumed silica nanoparticles noted A390 which exhibit interesting advantages such as high specific area, small particle size (7 nm), hydrophilic surface (high water retention) and low cost.

The idea is to combine the properties of organic and inorganic materials instead of polymers with both properties, which involves complex synthesis procedures. As a matter of fact, quite a few articles report on the use of poly(VDF-co-HFP) in composite materials to elaborate fuel cell membranes. Among them, Pereira et al. [31] synthesized an organic-inorganic hybrid membrane of poly(VDF-co-HFP) and mesostructured silica containing sulfonic acids groups using the sol-gel process. However, the ion-exchange capacity (IEC) was quite low (less than 0.4 meq/g) giving the fuel cells a lower performance of about 100 mV compared to Nafion 112<sup>®</sup>. In order to significantly increase the IEC value, Niepceon et al. [32] fabricated original sulfonated hybrid membranes based on heterogeneous poly(VDF-co-HFP)/nanosilica modified by poly(styrenesulfonic acid) and validated the use of core-shell like silica particles for proton-conducting membranes. These composite membranes exhibited proton conductivity values of 15–95 mS/cm at 20 °C and a power density of 1.0 W/cm<sup>2</sup> at 70 °C in single cell fuel cell tests with non-hydrated gas feeds. In order to obtain membranes performing at high temperature, Labalme et al. [33] developed hybrid membranes based on poly(VDF-co-HFP) and phosphonic polymers grafted onto silica nanoparticles.

The authors performed the 4-chloromethylstyrene radical polymerization, followed by the post-phosphonation of the polymers by the Mickaelis-Arbuzov reaction. The reaction was initiated by the chloromethylphenyltrimethoxysilane rendering it possible to graft the polymer onto the silica surface. The proton conductivity of the membrane based on 40 wt% loading in modified silica reached 65 mS/cm at 80 °C in liquid water and the corresponding hybrid membrane exhibited a good mechanical stability. However the main disadvantages of these procedures include the multi-step synthesis and the difficulty of controlling the polymerization.

Phosphonated membranes are mainly developed for automotive or for stationary applications which must be able to start at room temperature and operate in a broad range of temperatures. Indeed, above 100 °C important benefits may be generated for the fuel cell system: less sensibility to CO poisoning of the catalyst, less complex auxiliary system, better performance. But, very few studies present fuel cell tests and polarization curves of phosphonated membranes at these intermediate temperatures. This could be due to the difficulty of starting the fuel cell at room temperature and increasing the temperature until its operating conditions.

Some authors have proposed to use sulfonic and phosphonic acid bi-functionalized membranes in order to cover the temperature range [34]. However, the performance in fuel cells was found to be very low. Recently, triazole-based membrane doped with 13 wt% phosphoric acid was seen to operate in a wide temperature range (25–150 °C) with little humidification [35]. Specific gas diffusion electrodes with triazole-grafted polysiloxane electrolyte were fabricated in order to favor the membrane performance at high temperature. Here, the power density of the assembly was 180 mW/cm<sup>2</sup> at 80 °C and 210 mW/cm<sup>2</sup> at 150 °C under dry H<sub>2</sub>/O<sub>2</sub> gases.

The present article reports on a simple and fast preparation of hybrid membranes based on poly(VDF-co-HFP) and phosphonic polymers grafted onto fumed silica. As previously described, polymerization of diethylvinylphosphonate (DEVP) monomer can be obtained via anionic polymerization. Hübner et al. [36] recently demonstrated that chloromethylbenzyl groups can be used as termination agents. The idea presented in this work involved grafting the living polymers on chloromethylbenzyl-modified silica. This process should provide a much higher grafting density

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