Electronic Supplementary Information

for

Development of a fiber-based membraneless hydrogen peroxide fuel cell

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Fabrication process

Nanofibers fabrication

During electro-spinning process, the fine PVDF nanofibers form from a polymer solution with presence of mechanical stretch and high electrostatic field. Mechanical stretch is typically induced by using the rotatory collector in FFES or by moving the Taylor cone in NFES. In the past, different methods were introduced to fabricate PVDF nanofibers such as conventional far field electrospinning (CFFES) [1], modified far field electrospinning (FFES) [2] and near field electrospinning (NFES) [3, 4]. The main difference between these methods is the distance between needle and collector which is higher in FFES (around 100mm) as compare to NFES (around 1mm). Having a smaller emitting distance for fibers in NFES provides well aligned fibers with desired forms [7]. However, PVDF fibers which are electrospun by this method have a larger diameter (about 5 μm) and thus, are less flexible as compare to those fabricated by FFES method (about 1nm).

Fabrication of the PVDF single fiber

PVDF is a semi-crystalline polymer with a structure consisting of linear chains with sequence hydrogen and fluoride along with carbon backbone with a simple chemical formula (CH2–CF2). The chemical structure of PVDF falls between structure of Polytetrafluoroethylene (PTFE) which is (CF_2-CF_2) and Ethylene (CH_2-CH_2). While having close structure to Ethylene provides a great flexibility for PVDF, the crystalline similarity with PTFE gives stereochemical constraint to PVDF [5]. Due to this structural characteristic, PVDF forms in different crystal structures depending on sample preparation conditions. In nature PVDF appears in different phases which are known as α, β, γ and δ. Each of these phases is transferable to the others under certain external conditions. In general, α-phase is the most available phase in nature which typically obtained when the PVDF is cooled and solidified from melt. While the α-phase is known as a non-polar structure which does not show piezoelectricity, β-phase is understood as the only PVDF ferroelectric crystalline structure (polar) with strong piezoelectric effect. In general, high mechanical (approximately 50%) and electrical stretches (to align the dipoles) are required to predominantly convert the PVDF from α-phase to that of with β-phase. Table 1 provides crystallographic information of different PVDF crystalline structures [6].

Table 1. Crystallographic data of crystalline structures of PVDF [5]

	Unit cell	Space group	Molecular chain

α-phase	A=4.96Å, b=9.64Å, c(f.a)=4.96Å	$P2_1/c\text{-}C_{2h}^5$	$TGT\bar{G}$
β-phase	A=8.58Å, b=4.91Å, c(f.a)=2.56Å	$Cm2m\text{-}C_{2v}^{14}$	Slightly twisted planar-zigzag

Unoriented form of PVDF (α-phase) can be achieved by casting from solution of PVDF powder dissolved into acetone, and Dimethylacetamide (DMA). While the process of fabricating PVDF in α-phase is rather simple, more steps are required to achieve the nanofibers with β-phase. In the past various methods have been proposed to increase the ratio of the β-phase in the materials. For instance, annealing the sample at high pressure and high temperature or adding strongly polar hexamethylphosphorictriamide (HMPTA) in the solution.

Electrospinning of PVDF nanofiber

In this study, we used FFES process with a rotating collector to achieve aligned PVDF nanofiber and a stationary collector to electrospun chaotic nanofibers. There are various external parameters which have to be carefully optimized in order to achieve aligned PVDF nanofibers with very few beads. This section discusses the effect of electrospinning parameters on morphology and structure of the nanofibers. A careful and elaborate optimization of the electrospinning process parameters is conducted.

PVDF powder (MW 534000) is purchased from Sigma-Aldrich. For each electrospinning section a total of 1.7g PVDF is dissolved in a mixture of 3.5mL of DMF (VWR) and 8mL of acetone (VWR) and heated at 40°C for 120min so that the solution is homogeneous. The transparent viscous solution is transferred into a 1mL syringe for electrospinning. A voltage of 12kV is applied to the syringe needle, and a feed rate of 50L/min is used. The electrospun fibers are collected onto substrate, placed 15cm away from the needle, and the fibers are electrostatically aligned across the electrode gap. Effects of electrospinning parameters on electrospun nano fibers have been presented.

A: Solution preparation

Achieving a crystal form remarkably depends on solution preparation and electrospinning process parameters. In general, a polymer solution with very high viscosity causes more beads in the electrospun fibers and if the viscosity is even higher, the polymer solution may stuck the polymer in needle tip. Reducing the solution viscosity leads to fibers with smaller diameter and less beads. It has been reported that PVDF with concentration below 17 wt% is more likely to form beads with very less formation of fibers [7]. We investigated the effect of polymer concentration on PVDF nanofiber diameter for three different cases. In the first case, the solution was prepared by dissolving 1.2g PVDF in 3mL of DMF (VWR) and 8mL of acetone (VWR) PVDF. The polymer was dissolved at 70°C for 60min in a magnetic stirrer. For the second and third cases the PVDF ratio increased to 1.5g and 1.7g, respectively while the other effective parameters remained constant. Increasing the PVDF concentration in the polymer solution led to nanofibers with larger diameter. The reason for formation of more beads in lower concentration polymer solution is that in this case a higher mobility of the polymer chains occurs which causes stronger instabilities of jets during the electrospinning and induces higher stretching of the polymer and therefore, more beads appear[8]. On the other hand, higher PVDF concentration leads to a polymer solution with higher viscosity and more entanglements of the polymer chains which reduce the ability of the jet to stretch [7].

B: Electric field

As described before, electrospinning of PVDF requires high electric field to form the fibers in β-phase form. Change in voltage applied during the electrospinning is an important external parameter which can remarkably affect the surface and quality of fibers [9]. It is reported that change in the electric field applied during electrospinning process does not directly affect the morphology of the nanofibers for certain polymers however it can alter the shape and surface.

C: nozzle-to-collector distance

The distance between the nozzle and the collector is an important parameter which has influential effects on morphology and structure of the nanofibers because of their dependence on the deposition time, evaporation rate and whipping or instability interval[10]. It is reported that decreasing the nozzle to collector distance in electrospinning of PVDF might lead to an increase in fiber diameters [7]. However, our experiment did not show a significant difference in average diameter between the electrospun fibers developed with nozzle to collector distance of 100mm and 150mm.

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