Reactive Coaxial Electrospinning of ZrP/ZrO₂ Nanofibres

Surya Subianto^a, Anna Donnadio^b, Monica Pica^b, Sara Cavaliere^a, Mario Casciola^b, Deborah Jones^a, and Jacques Rozière^a ^aInstitute Charles Gerhardt, Equipe AIME, Université Montpellier 2, France ^bDipartimento di Chimica, Universita degli Studi di Perugia, Italy

Zirconium Phosphate (ZrP) have been investigated as filler materials for fuel cell membranes as they are good proton conductors that are chemically and thermally stable. Several studies have investigated the use of ZrP nanoparticles in composite membranes with Nafion and shown that they improve mechanical properties or proton conductivity above 100° C^{1,2}, while also reducing methanol crossover in direct methanol fuel cell applications.

However, in order to improve the performance of such composites, it is important to control not only the physical properties of the ZrP, but also to control the morphology in order to optimise its interaction with the polymer matrix. In this regard, previous studies on ZrP composites have used only nanoparticles, and no studies have investigated other 1D morphologies such as nanofibres which may provide stronger interaction and greater reinforcing effect.

More recently, electrospinning have gained significant interest in the fabrication of inorganic nanofibres due to its versatility, reproducibility, and the possibility of obtaining a mechanically robust mat of nanofibres. In general, a precursor solution or a nanoparticle dispersion is electrospun into fibres with the aid of a carrier polymer, with the inorganic fibres obtained after thermal treatment. Electrospun ZrO2 fibres have been obtained by this method³, however phosphoric acid is needed to form ZrP and as such direct electrospinning of ZrP nanofibres from precursor solutions have not been achieved. Furthermore, direct electrospinning of ZrP nanoparticles is difficult as they form a gel in the presence of water, impeding fibre formation.

In this presentation, we describe a novel method of fabricating ZrP nanofibres by reactive coaxial electrospinning. Coaxial electrospinning uses a coaxial needle with a core and a sheath solution which allows the co-electrospinning of separate precursor solutions, leading to the in situ formation of ZrP during the electrospinning process while keeping the carrier polymer concentration to a minimum. Through post-synthesis treatment, a ZrO_2/ZrP nanofibre mat can be obtained which shows nanofibres of much greater length than what would be achievable through conventional, chemical methods (Figure 1).



Figure 1. Electrospun ZrO2/ZrP fibres before (left) and after (right) thermal treatment

Such ZrP nanofibres would be ideal for use in a composite membrane with a proton conducting ionomer, as the fibre length and large surface area would provide a large interaction with the proton conducting matrix, while simultaneously acting as a mechanical reinforcement to the membrane.

1. D.J. Jones et al, Adv. Polym. Sci. 215 (2008) 219-264

2. M. Casciola et al, Fuel Cells 9 (2009) 394-400.

3. C. Shao et al, J. Crystal Growth 267 (2004) 380-384