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Qualitative spectroscopic characterization of the matrix–silane coupling agent interface across metal fibre reinforced ion exchange resin composite membranes☆

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ABSTRACT

The characterization of novel metal reinforced electro-dialysis ion exchange membranes, for water desalination, by attenuated total reflectance Fourier transform infrared spectroscopy mapping is presented in this paper. The surface of the porous stainless steel fibre meshes was treated in order to enhance the amount of surface oxide groups and increase the material hydrophilicity. Then, the metal membranes were functionalized through a sol–gel reaction with silane coupling agents to enhance the affinity with the ion exchange resins and avoid premature metal oxidation due to redox reactions at the metal–polymer interface. Polished cross sections of the composite membranes embedded into an epoxy resin revealed interfaces between metallic frameworks and the silane layer at the interface with the ion exchange material. The morphology of the metal–polymer interface was investigated with scanning electron microscopy and Fourier transform infrared micro-spectroscopy. Fourier transform infrared mapping of the interfaces was performed using the attenuated total reflectance mode on the polished cross-sections at the Australian Synchrotron. The nature of the interface between the metal framework and the ion exchange resin was shown to be homogeneous and the coating thickness was found to be around 1 μm determined by Fourier transform infrared micro-spectroscopy mapping. The impact of the coating on the properties of the membranes and their potential for water desalination by electro-dialysis are also discussed.

1. Introduction

Commercial thin film ion exchange membranes (IEMs) are composed of ion exchange resin (IEX) materials and can be used as fuel cells for energy generation or separation membranes for desalination by electro-dialysis (ED). IEMs consist of either a plain and dense plain ion exchange resin thin films or be structured as composite membranes from the impregnation or activation of an ion exchange resin across a porous substrate [1,2]. Recent studies demonstrated the potential of ceramics or metal nano-additives dispersed across the IEX material to enhance the electrical and mechanical properties of the membranes [3,4]. The presence of either nano-additives or a continuous conductive network increases the electrical conductance of the membranes reducing working currents while operating in ED, thereby reducing energy consumption and reducing the impact of membrane surface fouling on performance. The addition of the fillers also increased the materials resistance to abrasion, leading to stronger membranes [4] with the potential to be applied in industrial solvent reclamation and harsh environment desalination [5]. Porous metal frameworks exhibit superior electric and thermo-mechanical properties [6] offering complementary surrogates to fibrous polymeric material reinforcements used in the preparation of composite IEMs for water and industrial waste purification by ED [1,7]. The functionalization of metal surfaces is also a highly topical research area [6,8] due to the development of novel metal based or composite sensors, medical prosthesis and membranes [6]. It is, however, crucial to control the nature

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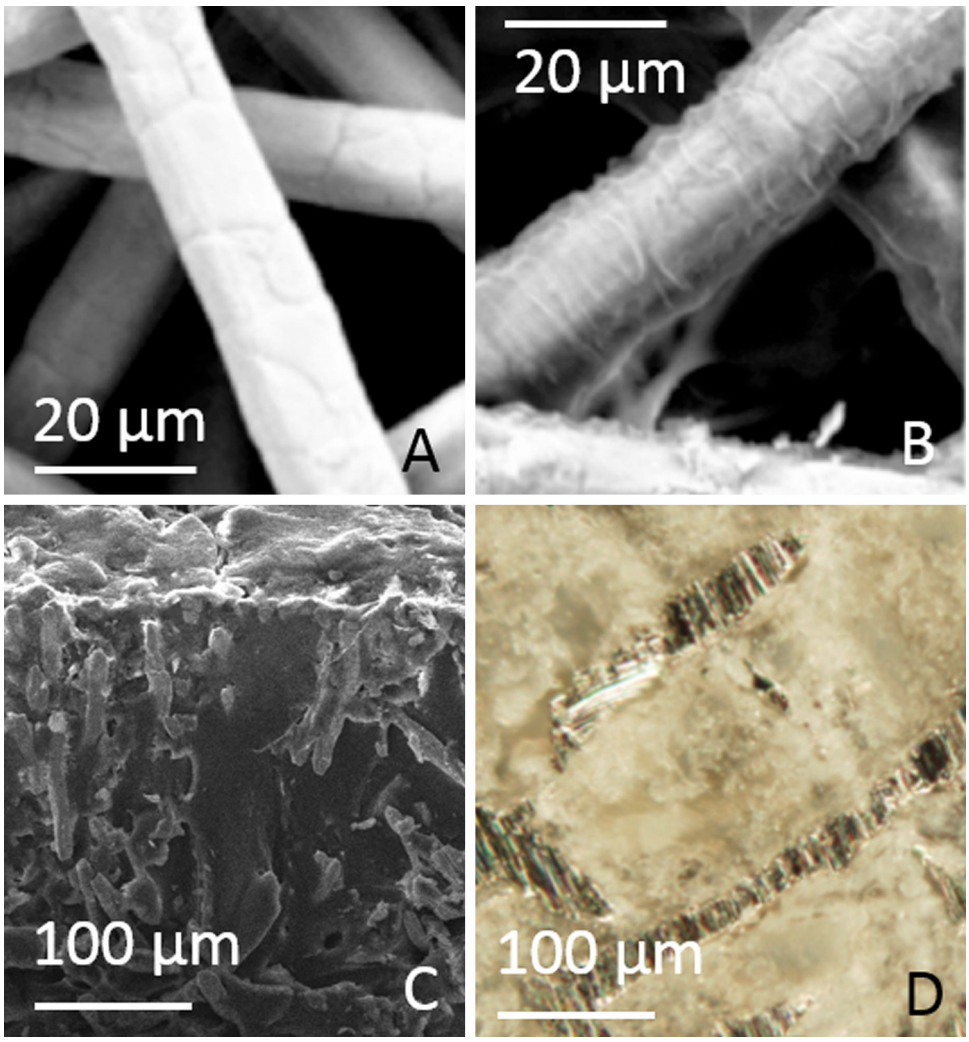

Fig. 1. Scanning electron micrographs (SEM) of (A) a pristine stainless steel fibre, (B) after amino-silane grafting, (C) of the composite membrane with embedded fibres across the IEX matrix and (D) optical micrograph of the surface of a polished sample for FT-IR analysis revealing individual fibres.

of the interface between the metal surface and the ion exchange material in order to prevent redox reactions that can result in degradation of both metal and poisoning of active ion exchange sites [1,9]. Advanced characterization techniques to evaluate the thickness, morphology and chemical nature of the interfaces across such composites are needed to improve understanding of diffusion mechanisms while performing ED [10,11].

In the present study, novel ion exchange metal composite membranes were fabricated and characterized to reveal the interface between the metal and the ion exchange resin material. The membranes were prepared by casting and activating an ion exchange resin across surface functionalized porous stainless steel frameworks. The first aim of the functionalization of stainless steel fibres composing of the substrates is to improve the adhesion between the ion exchange resins and the porous stainless steel fibre non-woven frameworks. The second objective is to provide a stable protective layer to perform the polymerization of the anion exchange resin for the preparation of stainless steel reinforced ion exchange membranes. The interface between the ion exchange resin, the silane coating and the metal surface was characterized by attenuated total reflectance (ATR) Fourier transform infrared (FTIR) mapping and the homogeneity of the composite membranes discussed. Eventually the anion and cation IEMs (AEM and CEM) were used in an ED setup to selectively remove dissolved sodium carbonate salts from a synthetic feed solution.

2. Materials and methods

2.1. Porous metal material

The metallic filter media were provided by BOSFA Pty Ltd. (Kewdale WA, Australia) part of Bekaert group. These stainless steel porous substrates were made of sintered metal fibres with standard 316SSL grade stainless steel. The diameter of the stainless steel fibres measured by scanning electron microscopy (SEM) was found to be 15 ± 0.5 µm (Fig. 1(A)).

2.2. Surface plasma treatment

The surface plasma treatments were performed at the Commonwealth Scientific and Industrial Research Organization (CSIRO), Materials Science and Engineering on a PICO G plasma rig (Electronic Diener GMBH, Germany). The stainless steel substrates were supported onto two stacks of piled up microscopy slides in order to expose simultaneously both sides of the substrates. This configuration was shown to allow for the generation of a homogeneous corona around the sample and to optimize the treatment efficiency. The plasma treatment conditions were fixed for samples preparation: water plasma under the discharge power of 80 W, total pressure of 0.2 mbar and treatment time of 5 min.