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Microstructured proton-conducting membranes by synchrotron-radiation-induced grafting

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ABSTRACT

Selective exposures of poly(ethylene-alt-tetrafluoroethylene) (ETFE) films with hard X-rays through high aspect ratio Ni-masks were performed at the LIGA3 beamline of the "Angström Quelle Karlsruhe" (ANKA) to create patterns of radicals used as initiators for the grafting of styrene into the bulk of the ETFE films. Grafted films were then sulfonated to obtain proton-conducting membranes. The structure definition, as investigated by scanning electron microscopy (SEM), showed a perfect discrimination between exposed and shaded areas through all the film thickness. Structuring results in a more homogeneous appearance of the membrane without affecting the degree of grafting and proton conductivity in the grafted areas. In fuel cell tests the structured membranes showed slightly lower performance due to 10% lower active area, but had a significantly higher lifetime.

1. Introduction

Exposure of polymeric material to ionizing radiation, such as X-ray, γ-ray or electrons, is a versatile method to tailor their physical and chemical properties [1]. Depending on the radiation energy, on the applied dose, and on the polymeric material, the latter can be cross-linked, degraded or chemically modified via grafting processes. Chain scission and cross-linking processes change properties of polymer materials without changing their overall composition and are widely used in the industry for applications, such as wire insulations [2], heat shrink products [3], sterilization treatments [4], and for enhancing the processing characteristics of polymers [5]. In contrast, the chemical modification process via a grafting reaction allows introducing special characteristics of one polymer into another [6]. Upon exposure with high-energy ionizing radiation, radicals are created in the bulk of a polymer material and are transformed into stable radicals when in contact with oxygen of the ambient air. Those radicals are then used as radical initiators for the grafting of a second polymer, to create for example ion-exchange membranes [7].

Radiation-grafted membranes are considered to be low-cost alternatives for Nafion® membranes that are commonly used in fuel cells [8–13]. However, during the grafting process the mechanical stability of the base polymer deteriorates, limiting the use of these membranes. Using lithographic X-ray exposures to limit the grafting to defined areas in the fluoropolymer base film while leaving other parts of the film intact can offer a solution to this problem [14]. With this approach, the grafted areas can provide the required ionic conductivity while the remaining areas maintain the mechanical stability.

In deep X-ray lithography, high-energy synchrotron radiation is used to create high aspect ratio polymer structures with extremely sharp, smooth and vertical sidewalls [15]. Exposure of thick spin-coated polymer films though a metal absorption mask is used to crack the polymer in the exposed areas into soluble pieces removable by a solvent (developer). The so-called LIGA process [16,17] combines a deep X-ray lithographic irradiation with galvanic filling of the structures and subsequent replication steps and is used to manufacture micro- and micro-opto-electromechanical systems (MEMS and MOEMS) or micro-fluidic systems [18].

The LIGA process requires long exposure times, i.e. in the range of minutes to hours to reveal a pattern by cracking a polymer film into soluble pieces. In contrast exposure of a polymer film in the range of a few seconds by such high flux X-ray sources is expected to be sufficient to create patterns via graft-polymerization, since every radical formed inside the film can lead to the formation of a polymer chain.

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To our knowledge, this work is the first report on the combination of high-energy synchrotron lithographic exposures of polymer films with subsequent bulk grafting reactions. The work addresses the question whether high aspect ratio structures grafted inside polymer foils could be obtained with accuracy similar to established deep X-ray lithographic processes. Furthermore, we investigated the effect of the structuring on the achievable degree of grafting, the proton conductivity, the mechanical properties, and on the membrane performance in single H_2/O_2 cell tests.

2. Experimental

2.1. Materials

Extruded 25- and 100-μm-thick films of poly(ethylene-alt-tetrafluoroethylene) (ETFE, Nowoflon ET-6235 Nowofol GmbH, Siegsdorf, Germany) were washed in isopropanol and in acetone.

Styrene (Fluka), divinyl-benzene (Fluka), isopropanol (Fischer), toluene (Fischer), acetone (Fischer), caesium chloride (Fluka), dichloromethane (Fischer) and chlorosulfonic acid (Fluka) were used as received. Pure water with a resistance of 18.1 MΩ/cm was utilized.

2.2. Fabrication of high aspect-ratio nickel masks

High aspect ratio nickel grid microstructures were fabricated by a lithographic procedure (Fig. 1). A 100-μm-thick SU8 resist layer was spin-coated on a silicon wafer on which a 100-nm-thick titanium layer was evaporated. The resist layer was then exposed using UV light (λ = 365 nm) through a quartz mask with chromium grid structures. After development of the exposed SU8 resist, nickel was electroplated in the SU8 mould. The Ni-SU8 membrane was then separated from the wafer by sonication in acetone, which resulted in a 150-μm periodic grid nickel structures with 15-μm wide and 85-μm high features embedded in a 100-μm-thick SU8 layer.

2.3. Exposure

ETFE films were exposed at the LIGA3 beamline of the "Angströmquelle Karlsruhe" (ANKA) through the high aspect ratio nickel shadow masks (Fig. 1) with hard X-ray photons produced by a bending magnet. The incident radiation was first filtered through

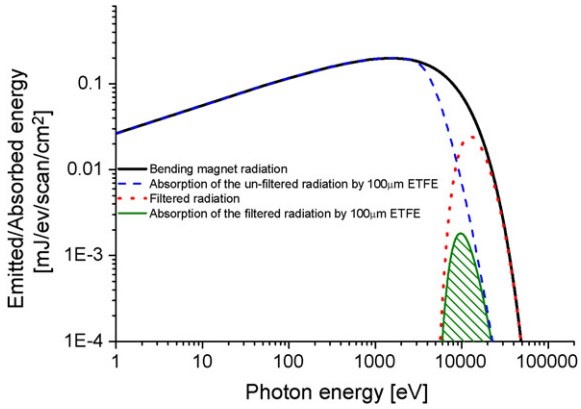

Fig. 2. Emitted energy spectrum from the bending magnet (a, ▬) and absorbed energy by a 100-μm ETFE foil (b, ▬ ▬). Filtered beam (c, ▪ ▪ ▪) and absorbed energy by a 100-μm ETFE foil placed after the filters (d, filled curve, ▬).

225 μm of beryllium, 83 μm of aluminium and 696 μm of carbon foils in order to stop most of the low energy photons (<8 keV) of the beam (Fig. 2). The Ni-grid was packed between two 25-μm-thick Kapton foils, to trap secondary electrons produced during the exposure. Either six pieces of 25-μm or two pieces of 100-μm-thick ETFE, with dimension of 6 cm × 6 cm, were placed as close as possible to the nickel grid to avoid blurring of the shadow image. The films were placed such that their machining direction was parallel to the grid structure. The same number of films was also placed in front of the mask to get uniformly exposed areas. This stack (membranes-Ni-grid-membranes) was then fixed onto the scanning stage. The exposure chamber was closed, pumped down and filled with 100 mbar of Helium. The stack was scanned several times through the X-ray beam to obtain defined exposure doses in the range of 0.7–4.5 kGray. After the exposure the films were cooled with dry ice to prevent the deactivation of the radicals and stored in a deep freezer (−80 °C) until further processing.

2.4. Grafting reactions

The irradiated ETFE films were grafted using a solution of styrene (19%$_{vol}$) as a monomer and divinyl benzene as a cross-linker (1%$_{vol}$) in an isopropanol (70%$_{vol}$) and water (10%$_{vol}$) mixture. The grafting

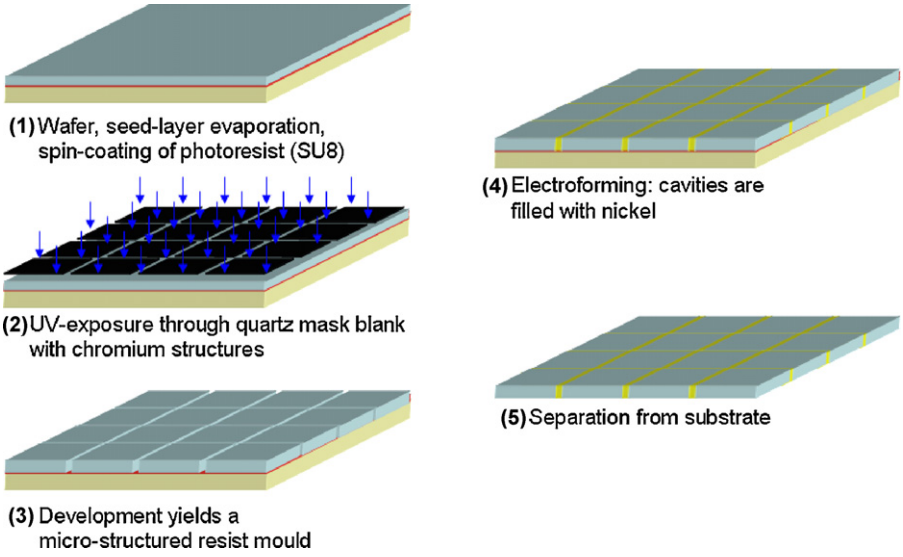

Fig. 1. Production process scheme of the nickel shadow masks.