Radiation Physics and Chemistry 135 (2017) 133–141

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Mask-assisted electron radiation grafting for localized through-volume modification of porous substrates: influence of electron energy on spatial resolution

A. Forner-Cuenca[a], V. Manzi-Orezzoli[a], P.M. Kristiansen[b,c], L. Gubler[a], T.J. Schmidt[a,d], P. Boillat[a,e,*]

[a] *Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
[b] *INKA Institute of Polymer Nanotechnology, FHNW University of Applied Sciences and Arts Northwestern Switzerland, School of Engineering, 5210 Windisch, Switzerland*
[c] *Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
[d] *Laboratory of Physical Chemistry, Department of Chemistry & Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland*
[e] *Neutron Imaging and Activation Group, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

A R T I C L E I N F O

Keywords:
Electron radiation grafting
Monte Carlo simulation
Porous material
PEFCs
Patterned wettability

A B S T R A C T

The spatial resolution aspects of the local modification of porous materials by electron induced graft-polymerization were studied by a combination of experiments and numerical simulations. Using blocking masks, only selected regions of the material were exposed to radiation and subsequently grafted. The main focus of this study is the application to gas diffusion layers, a carbonaceous ~200 µm thick porous substrate widely used in fuel cells, with the goal of improving water management by locally tuning the wettability. The comparison of experiments performed with different electron energies and corresponding simulations shows good agreement, identifying the energy threshold necessary to graft through the material to be approximately 150 keV. The impact of electron energy on spatial resolution was studied, showing that the blurring effects due to electron scattering reach a maximum at around 200 keV and are reduced at higher electron energies. Finally, the numerical simulations were used to define the conditions necessary to selectively graft only parts of bi-layer fuel cell materials.

1. Introduction

In the last 70 years, the use of electron beam technologies has impacted various fields, such as micro and nanofabrication (Geissler and Xia, 2004; Shore, 2013; Chen, 2015; Padeste and Neuhaus, 2015), electron microscopy, curing (Wolff-Fabris et al., 2011; Drobny, 2013a, 2013b) and welding (Sun and Karppi, 1996), among others. Electron-beam lithography (EBL) is a technique based on the use of a focused electron beam to draw custom shapes into so-called resist layers, i.e. an electron-sensitive material, which undergoes either chain scission (polymethyl methacrylate (PMMA)) or cross-linking (e.g. SU-8) upon electron exposure and allows for pattern definition by selective removal of the irradiated (or non-exposed) fraction of the resist upon development. EBL is nowadays used in a number of applications and has been developed over the years to manufacture sub 10 nm resolution structures (Vieu et al., 2000; Altissimo, 2010). Due to the demanding technology required to focus the beam, EBL is a very costly technique (> 2 M$/device (Altissimo, 2010)). There are, however, other applications that do not require such narrow structures. There have been recent works, mainly in the field of microfluidics, focusing on the production of patterns on a scale of tens to hundreds of micrometers using different technologies, such as plasma (Garrod et al., 2007), UV irradiation (Zahner et al., 2011), among others. To the best of our knowledge, none of these studies have focused on modifications of thick porous materials (thickness > 100 µm) using electron beams, which we address in this work. (Fig. 1).

Our group has recently developed a method to modify porous gas diffusion layers (GDLs) used in polymer electrolyte fuel cells (PEFCs) (Pasaogullari and Wang, 2004; Cindrella et al., 2009). The method is based on electron radiation grafting of the polymeric coating covering the carbon fibers (Boillat et al., 2014; Forner-Cuenca et al., 2015). The grafting polymerization refers to the formation of a copolymer between the original polymer (pA) and a newly added monomer (M) (Stannett, 1990; Dargaville et al., 2003; Gubler et al., 2005). The resulting molecular structure can be written as pA-*g*-pM. Normally, pA is a low cost structural polymer and M introduces an additional valuable

* Corresponding author at: Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland.

http://dx.doi.org/10.1016/j.radphyschem.2017.01.036
Received 24 September 2016; Accepted 27 January 2017
Available online 28 January 2017

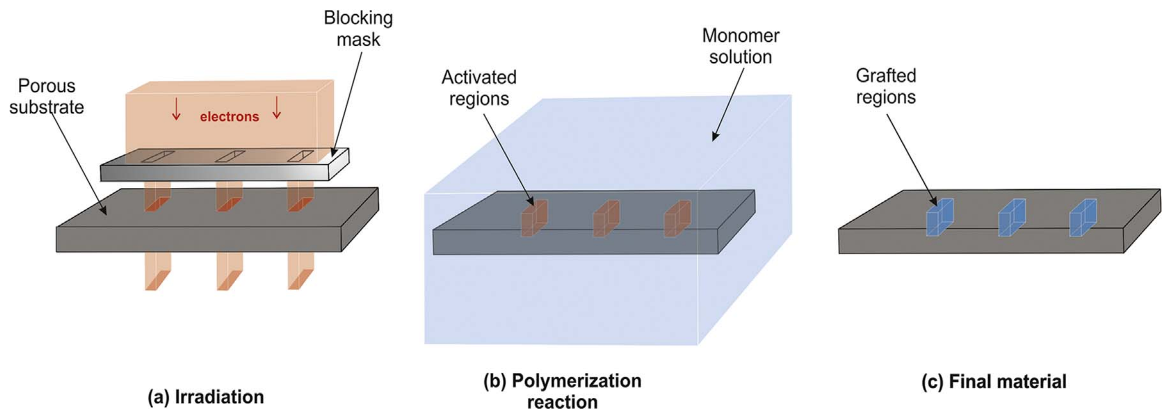

Fig. 1. Illustration of the synthetic process to obtain porous substrates with structured properties. (a) electron radiation using a blocking mask; (b) activated material is brought into monomer solution; (c) finally, a material with localized grafted regions is obtained.

property. In our particular case, pA is a hydrophobic polymer (fluorinated ethylene propylene copolymer (FEP)) and M is a hydrophilic compound (here acrylic acid) to increase the wettability. Details on the chemical structures and polymerization reactions can be found in our previous work (Forner-Cuenca et al. 2016a). Since the minimum expected pattern width to be produced is in the range of 100 µm, we use masks to block the radiation in the undesired regions. By adequately selecting the electron energy the beam should penetrate the entire material thickness, generating radicals in the polymeric coating located under the mask-free regions. In a subsequent step, the activated materials are brought in contact with a liquid solution containing the hydrophilic monomer and the grafting polymerization starts on the activated regions. The control of the experimental conditions (type of monomer, concentration, solvent, temperature, reaction time, etc.) allows for tuning the desired final properties (Forner-Cuenca et al. 2016a).

While a number of fields could benefit from the work on modifying thick porous substrates, the implementation of GDLs with patterned wettability in PEFCs is expected to improve the complex water management by providing optimized liquid/gas transport characteristics (Ji and Wei, 2009). We have demonstrated significant fuel cell performance increase when using the novel GDLs using the mask-assisted radiation grafting method (Forner-Cuenca et al., 2015, 2016b, 2016c). The objective of this paper is to provide a more fundamental understanding on how the radiation dose is distributed and, from this knowledge, set the guidelines to produce a second generation of GDLs with patterned wettability with higher resolution and tailored penetration depth.

We start by comparing experimental results of elemental analysis on top and bottom surfaces with Monte Carlo simulations of electron transport in a reproduced geometry. In these lines, we compare the achieved resolution as a function of the electron energy and discuss the 2-dimensional dose distribution. Afterwards, the effect of separating the mask and the substrate is studied experimentally for different distances. Simulations provide a theoretical basis of the forward scattering phenomena at two energies. Further, we theoretically explored the impact of backscattering by using different materials on the back-side of the substrates. The paper closes by presenting an example of the use of simulations in a predictive way by irradiating a bi-layer material to a pre-selected penetration depth.

2. Experimental methods and simulations

The experiments are used to quantify the distribution of grafted molecules on top and bottom surfaces, and the simulations to calculate the absorbed dose distribution through the thickness of the material as well as to extrapolate the results to ranges of energies not accessible with the currently used electron sources. The experimental methodology consists of the following steps: (I) GDLs are electron beam irradiated using masks; (II) activated GDLs react with the monomer, acrylic acid; (III) grafted GDLs are cleaned and exposed to sodium hydroxide (NaOH) in order to replace the protons in the acid groups by a sodium ion (Na^+) for visualization purposes; (IV) elemental mappings are recorded using energy dispersive X-ray analysis; (V) elemental mappings are processed and profiles of the grafting yield are obtained. The following subsections introduce the materials, procedures and techniques used, alongside with details of the Monte Carlo simulations.

2.1. Materials

2.1.1. Masks

2 mm thick stainless steel masks were used. Rectangular openings were machined using a pressurized water jet (WATERjet, Aarwangen, Switzerland). Two types of masks were used for the studies reported herein: (1) a mask containing rectangular slits of 0.5 mm width spaced 5 mm; (2) a mask with two perpendicular rectangular slits (500 µm width) forming a cross-like shape. The first mask was used for the studies about penetration depth and resolution, while the second mask was used for the beam broadening study to elucidate beam divergences in different spatial directions. The slits of mask (I) were placed in the direction parallel to the linear electron beam axis.

2.1.2. Gas diffusion layers (GDL)

Untreated Toray Paper 060 (TGP-H-060) was used as base GDL material (purchased at Fuel Cell Earth Store). It has a thickness of ~200 µm, a bulk density of 0.44 g cm^{-3} and a porosity of ~78%. The material was coated with FEP using the “dipping” method followed by a thermal treatment. The details about the coating application were described elsewhere (Forner-Cuenca et al., 2015, 2016a). For this particular study, a coating load of 70% (weight of the coating relative to the base material) was used. We decided to use a high coating load to have a sufficient amount of polymer to perform elemental mappings with a good image quality.

2.1.3. FEP films (as dosimeters)

Fluorinated ethylene propylene (FEP) films of 25 µm thickness were used (DuPont™ Teflon® FEP Gauge 100) for measuring the beam width in the beam broadening study (Section 3.3). The foils were cut into pieces of 6 cm×6 cm and rinsed with abundant ethanol to remove any contaminant present. Afterwards, they were dried at 60 °C in vacuum overnight before being packed into bags.